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Dinuclear Metal Complexes, Part IX, Copper(II), Nickel(II) and Cobalt(II) Complexes with a Schiff-base Derived from 3-formylsalicylic Acid and Carbohydrazide

K.C. SATPATHY,* A.K. PANDA, A. MAHAPATRA AND B. MISHRA
P.G. Deartment. of Chemistry
Sambalpur University
Jyoti-Vihar-768 019, India.

Copper(II), nickel(II) and cobalt(II) complexes of the type $[M\ (3\text{-fsaH})_2CAR(H_2O)_n]$ and $[M_2\ (3\text{-fsa})_2\text{-}CAR(H_2O)_n]$ where $(3\text{-fsaH}_2)_2\text{-}CAR$ is a Schiff-base derived from 3-formylsalicylic acid and carbohydrazide, $n = 0, 1, 2$ or 3 etc., have been isolated and characterised on the basis of physico-chemical methods. The antiferromagnetic character of dinuclear copper(II) complex has been revealed from the magnetic and ESR spectral data. The dinuclear cobalt(II) complex has been found to have a mixed-spin state comprising of a high-spin and a low-spin cobalt(II) ion. Also the dinuclear nickel(II) complex exhibits a slightly lower magnetic moment value corresponding to two unpaired electrons. The mononuclear copper(II) and cobalt(II) complexs are paramagnetic unlike the mononuclear nickel(II) complex. The reflectance spectra of all the complexes are consistent with the observed magnetic moment values. Infrared spectra, thermal analysis and molar conductivity values are in complete agreement with the proposed structure. The mono and dinuclear copper(II) complexes exhibit maximum fungitoxicity in comparison to the corresponding cobalt(II) and nickel(II) complexes.

INTRODUCTION

Polynuclear metal complexes containing two homo or hetero metal ions are of interest in connection with spin exchange and charge transfer between metal ions and in the domain of metalloenzymes and homogeneous catalysis. The synthesis of homo polynuclear complexes involve choosing of a suitable ligand which can coordinate to more than one metal centre. But the synthesis of heteropolynuclear complexes involves a step wise reaction process.

The Schiff-base derived from 3-formylsalicylic acid and diamines have been widely used in the preparation of homo di and mononuclear complexes[1], heterodinuclear complexes[2], and mixed spin complexes[3]. As a continuation of our previous work[4–8] of isolating systems with multi metal centres and strong magnetic interactions, some mono and dinuclear metal complexes with a Schiff-base derived from 3-formylsalicylic acid (3-fsaH_2) and carbohydrazide are reported in the present communication. The metal ions of the complexes are expected to have different stereochemistries and spin state.

RESULTS AND DISCUSSION

The mono and dinuclear complexes isolated have the composition $[M\,(3\text{-fsaH})_2\ \text{-(CAR)}\ (H_2O)_n]$ and $[M_2\,(3\text{-fsa})_2\text{-(CAR)}\,(H_2O)_n]$ respectively, where $(3\text{-fsaH}_2)_2\text{-CAR}$) is a Schiff-base derived from the condensation product of 3-fsaH_2 and carbohydrazide, n = 0, 1 or 3 etc. The complexes are highly coloured and sparingly soluble in common organic solvents. The solubility exceeds to a considerable extent with solvents like DMF and DMSO suggesting them to be non-electrolytes. Most of them decompose above 250°C before melting.

IR Spectra

Since it was not possible to isolate the Schiff-base ligand, the spectra of the complexes were compared with the starting materials and other related compounds. Since both the series of complexes exhibited and identical pattern, we are of the opinion that the complexes of each series are isostructural.

The ligand moiety is expected to function as dianionic and quadrianionic for mono and dinuclear complexes respectively, which may be represented in either of the following structures [Fig. 1 (a) and (b)].

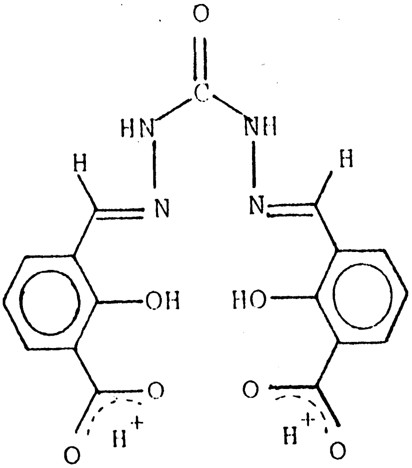


Fig. 1 (a)

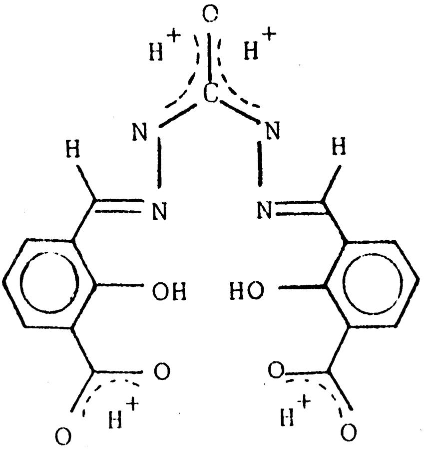


Fig. 1 (b)

A strong doublet at *ca.* 1635 and 1640 cm^{-1} in all the complexes has been attributed to ν(C=N) vibration. The position of this band, at a comparatively higher frequency than the usual ν(C=N) value, led us to suggest that the azomethine group has taken part in complexation[9] and the splitting suggests the presence of azomethine group in different chemical environment.

It is known[10, 11] that the stretching frequency of ν(C=O) increases in a complex if it is not coordinated. Thus, the band observed at *ca.*, 1745 cm^{-1} may be assigned to ν(C=O) corresponding to the ν(C=O) band observed at *ca.*, 1735 cm^{-1} in the free carbohydrazide molecule.

The hypsochromic shift of the band due to ν(C—OH) at 1320 cm^{-1} indicates that deprotonated phenolic —OH has participated in complexation[12]. The large separation of the two bands at *ca.* 1610 and 1345 cm^{-1} ($\Delta COO^- = 265\ cm^{-1}$), is indicative of the monodentate nature of the carboxylate group[13]. However, the band for carboxylate group remain undisturbed in the IR spectra of the mononuclear complexes.

In the high frequency region, a broad band centered at *ca.* 3480 cm^{-1} has been assigned to the presence of coordinated water molecules[14–17], a fact further strengthened by the additional band at *ca.* 845 cm^{-1}.

The coordination of the metal ion through the carboxylic/phenolic oxygen and azomethine nitrogen atoms is further confirmed by the appearance of additional bands in the region 440 and 480 cm^{-1} attributed to ν(M—N) and ν(M—O) respectively[17, 18].

Thermal Analyses

In order to ascertain the nature of water molecules, as indicated in the IR spectra, thermal analyses was undertaken. Mononuclear complexes loose weight at *ca.* 85°C with a broad endothermic peak at the same temperature in the DTA curve. The weight loss corresponds to two and one molecule of water of crystallisation[19, 20] for copper(II) and nickel(II) complexes respectively. The first weight loss corresponding to the loss of one molecule of water for mononuclear cobalt(II) complex was encountered at *ca.* 140°C supported by an exothermic peak at the same temperature, is the characteristics of coordinated water.

Dinuclear complexes exhibited the characteristics of water of crystallisation as well as coordinated water. The loss of water of crystallisation range from 60° – 80°C. Elimination of coordinated water for copper(II) and nickel(II) complexes occurred in a single step supported by a broad endothermic peak at *ca.* 135°C and at *ca.* 140°C respectively. Simultaneous elimination of coordinated water suggests that they are in the same chemical environment[21]. However, the dinuclear cobalt(II) complexes lost water molecules in two steps, one at *ca.* 135°C *corresponding to the loss of one molecule of coordinated water (exactly at the same temperature as the mononuclear cobalt(II) complexes) and the other at ca.* 148°C corresponding to the loss of two molecules of coordinated water. Both the series of complexes finally decompose to their metal oxides. The thermal stability of the complexes in each series is in the order of Co > Ni > Cu.

Electronic Spectra and Magnetic Properties

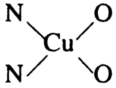
Mononuclear Complexes: The electronic spectrum of the nononuclear copper (II) complex has a ligand field band at 18,084 cm^{-1}, the position of absorption being in agreement with the band for N, N′-salicyledeneethylenediaminato copper(II)[22], with the same N_2O_2-chromophore. This absorption can be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition. The room temperature magnetic moment value of 1.91

BM, also imply that the copper(II) ion of the present complex has a planar structure similar to the corresponding N, N′-salicyledeneethylenediaminato copper(II) complex.

The reflectance spectra of the mononuclear nickel(II) complex exhibit a single ligand field band at ~ 18,480 cm^{-1} which is in agreement with the band for N, N′-salicyledeneethylenediaminato nickel(II)[22] complex with a planar N_2O_2-coordination. Hence it is imperative that the present mononuclear nickel(II) complex has also a planar environment around the nickel(II) ion. This fact is further supported by the diamagnetism of the nickel(II) complex.

It is[23] known that N,N′-disalicyledeneethylenediaminato cobalt(II), [Co (salen)], reacts with pyridine(py) to form, [Co (salen) (py)], where the cobalt(II) ion is in low-spin state with a tetragonal-pyramidal geometry and has reflectance bands at 6000, 9000, 13500 and 16000 cm^{-1}. The fact that the present mononuclear cobalt(II) complex also exhibits bands at 5990, 8980, 13460 and 15950 cm^{-1}, with a room temperature megnetic moment value of 1.94 BM in accordance with the cobalt(II) ion in low-spin state; suggests that the mononuclear cobalt(II) complex may also have a similar tetragonal-pyramidal structure, with a water molecule occupying an apical position, since pyridine does not differ much from water in ligand field strength[24].

Dinuclear Complexes: The electronic spectral data and the room temperature magnetic moment values of this series of complexes are different from those of the mononuclear complexes.

Two bands are observed in the reflectance spectrum of the dinuclear copper(II) complex in the visible region. The high energy band corresponds well with the band for CuH_2fsa-en (where H_2fsa-en is a Schiff-base derived from 3-formylsalicylic acid and ethylenediamine). The position of this band is practically similar to the band for N, N-disalicyledene-*o*-phenylenediaminato copper(II)[14]. Therefore, this band was tentatively assigned to the inner copper(II) which possess an N_2O_2-chromophore. Sinn *et al.*[22] have observed that dichloro [N, N-disalicyledenetrimethylenediaminato copper(II)] has a d-d band at 17,100. This suggests that the coplanarity of the unit  in [N,N-disalicyledemetrimethylenediaminato copper(II)] is enhanced on forming a dinuclear complex bridged by phenolic oxygen. Therefore, the band at 17,760 cm^{-1}, found in the reflectance spectrum of our present complex is attributed to Cu-N_2O_2 chromophore. On the other hand, the lower energy band at 15,200 cm^{-1} is tentatively assigned to the 'outer' copper(II) ion. Transitions involving the 'inner' and 'outer' copper(II) ions have been tentatively assigned to $^2E_g \rightarrow {}^2T_{2g}$. The room temperature magnetic moment value of 0.72 BM is subnormal, which may be due to super exchange through the P_π-orbital of the oxobridge.

The reflectance spectrum of dinuclear nickel(II) complex exhibits three d—d bands. The band at *ca.* 18,380 cm^{-1} is well in agreement with the band for mononuclear nickel(II) complex. The rest two band at *ca.* 14,925 and 9,980

cm^{-1} indicates the presence of a nickel(II) ion in an octahedral environment. Accordingly coordination of two water molecules from apical positions have been suggested for the 'outer' nickel(II) ion. The bands at *ca.* 9.980 and 14,925 cm^{-1} are assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions respectively.

Magnetic moment per nickel(II) ion has been observed to be lower than the spin-only value. This may be possible either by antiferromagnetic spin-pairing between two paramagnetic nickel(II) ions or a formation of a complex with one diamagnetic and one paramagnetic nickel(II) ions. The later possibility seems more reasonable from our observation of the electronic spectra.

The ligand field band of dinuclear cobalt(II) complex is complicated exhibited several absorption bands in the region 6000 to 20,000 cm^{-1}. It has been already established that the complex CuCo(3-fsaR) $(H_2O)_{2-3}$ [where R is a diamine] has the outer cobalt(II) ion in a pseudo-octahedral environment[2] with water molecules from apical positions. Hence, it is likely that the 'outer' cobalt(II) ion is our present dinuclear cobalt(II) complex also has a pseudooctahedral structure coordinated by water molecules from apical position. It is known[23] that N, N-di-salicyledenediaminato cobalt(II), [Co(salen)] reacts with pyridine(py) to form [Co(salen) (py)]; where the cobalt(II) ion is in low-spin state and has a tetragonal-pyramidal geometry with pyridine at the apex. Therefore, it seem reasonable that the complex, [Co{(3-fsa)$_2$-CAR} $(H_2O)_3$], we have isolated has a dinuclear structure composed of a 'inner' low-spin tetragonal pyramidal and spin free 'outer' pseudooctahedral cobalt(II) ion (because pyridine does not differ much from water in the ligand strength).

The complex CuCo(3-fsa-R) $(H_2O)_{2-3}$ (where R is a diamine like ethylenediamine, propylenediamine etc) exhibits reflectance bands[3] at *ca.* 8,300, 11,000 and 19,200 cm^{-1}. On the other hand the spectrum of 'inner' cobalt(II) in [Co$_2${(3-fsa)$_2$-CAR]}$(H_2O)_3$] should be similar to that of [Co(salen) (py)] which has d—d bands at *ca.* 6000, 9000, 13,500 and 16,000 cm^{-1} [24, 25]. The reflectance spectra of dinuclear cobalt(II) complex, [Co$_2${(3-fsa)$_2$-CAR}$(H_2O)_3$], shows five bands at *ca.* 6890, 8450, 12,370, 16,250 and 18,330 cm^{-1}. This can be interpreted in terms of the superimposition of the spectra of the five-coordinated 'inner' and six-coordinated 'outer' cobalt(II) ions. Hence, no conclusive assignment of the bands could be made.

The magnetic moment of [Co$_2$ {(3-fsa)$_2$-CAR} $(H_2O)_3$] at room temperature has been found to be 4.89 BM. Since low-spin cobalt(II) and high-spin cobalt(II) (octahedral) have magnetic moments in the range of 1.9 to 2.8 BM and 4.3 to 5.2 BM respectively[26]; the magnetic moments expected for high-spin dinuclear cobalt(II), mixed-spin dinuclear cobalt(II) and low spin dinuclear cobalt(II) complexes are in the range of 6.1 to 4.7, 4.7 to 5.9 and 2.7 to 4.00 BM respectively, provided that no spin-exchange interaction in operating between the cobalt(II) ions. Thus the present complex may be mixed-spin dinuclear or magnetically coupled high spin dinuclear. As already discussed, the electronic spectra favours the mixed-spin dinuclear structure.

ESR Spectra

The ESR spectral data of the mono and dinuclear copper(II) complexes have been presented (Table-1).

TABLE-1

Complexes	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
[Cu {(3-fsa)$_2$-CAR}] $(H_2O)_2$	2.28	2.08	172	67
[Cu$_2$ {(3-fsa)$_2$-CAR}.$(H_2O)_2$] $(H_2O)_2$	2.23	2.12	140	95

($A_{\parallel}$ and $A_{\perp}$ values in gauss)

In case of the mononuclear copper(II) complex the observed $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$ values corresponds to a near square-planar geometry around the copper(II) ion[29]. The $g_{\parallel}$ and $g_{\perp}$ values of the dinuclear copper(II) complex are closer as compared to the mononuclear one, suggesting a distorted octahedral geometry around the metal ions. Since the 'inner' copper(II) ion with N_2O_2-chromophore has been established to be near square-planar, we are of the opinion that the 'outer' copper(II) ion may have a pseudooctahedral arrangement around it with two water molecules occupying the apical positions[30].

As the magnetic moment data of the dinuclear copper(II) complex suggest the presence of a strong magnetic interaction between the metal ions, the metal-metal distance (R) has been computed from the ESR spectral data[31]. The value of R has been computed to be 3.4°A, which is much less than the limit value (4°A), further strengthening our contention of the antiferromagnetic character of the complex.

On the basis of the above discussion, we propose the following structure of the mononuclear (Fig. 2) and dinuclear (Fig. 3) complexes which satisfies all our observations.

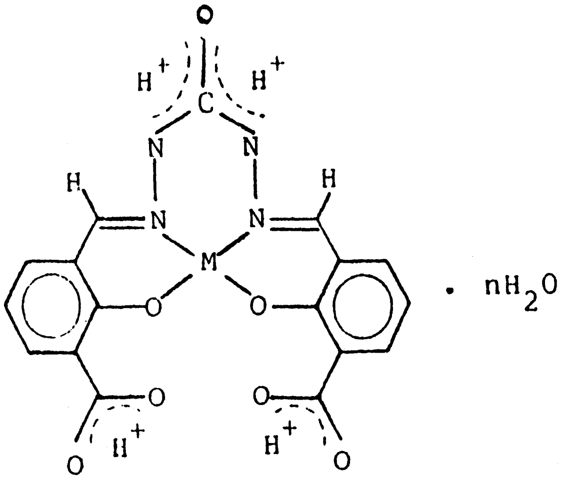


Fig. 2 [M = Cu(II), Ni(II) or Co(II)

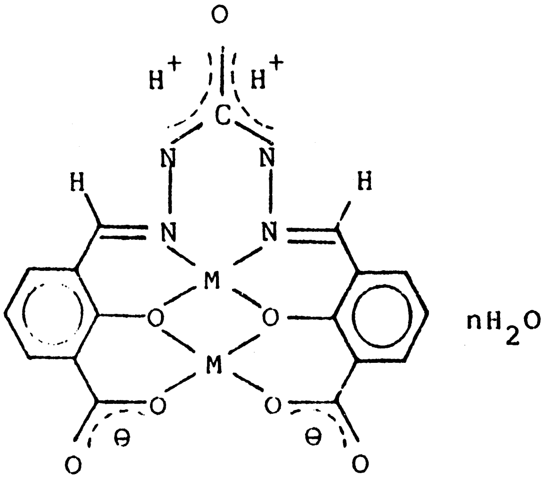


Fig. 3 [M = Cu(II), Ni(II) or Co(II)

EXPERIMENTAL

3-Formylsalicylic acid (3-fsaH_2) was prepared following the literature method of Duff and Bills[27], while carbohydrazide was prepared as per the literature method[28].

Since the Schiff-base ligand could not be isolated, both the mononuclear and dinuclear complexes were prepared *in situ* by taking different amounts of the metal salts while keeping the carbohydrazide stoichiometries constant.

Preperation of mononuclear copper(II) complex: An aqueous solution of copper(II) acetate (1m) added to an aqueous mixture (30 mL) of sodium carbonate (1m), 3-fsaH_2(2m) and carbohydrazide (1m) gently. The resultant solution was heated to 60°C on a waterbath for about 10 min when microcrystalline solids slowly appeared. The precipitate was filtered, throughly washed with hot water and dried in vaccum.

The dinuclear nickel(II) and cobalt(II) complexes were isolated in an identical manner. The analytical data of the complexes have been presented in Table-2.

Fungicidal Screening

All the complexes have been screened as possible fungitoxides against the fungal pathogens *Helminthosporium Oryzae* and *Fusarium Oxysporium.* The screening has been carried out according to the Horsfall method[32] in different concentrations. The amount of germination or growth inhibition was determined after inoculation of the fungal spores onto Czapexdox agar-agar media. Spores were also inoculated onto the agar-agar media containing the test sample. The whole system was kept in an incubator for five days. The percentage of inhibition was calculated as follows,

$$\% \text{ of inhibition} = 100(P - Q)/P$$

where P = area of colony growth without test sample and Q = area of colony growth with the test sample. The results have been presented in Table-3.

TABLE-2
ANALYTICAL DATA OF THE COMPLEXES DERIVED FROM 3-fsaH2 AND CARBOHYDRAZIDE

Complexes	μ_{eff} (B.M.)	Decomposition Temperature	% Found (Calcd.)			
			M	C	H	N
$[Cu_2\{(3\text{-fsa})_2\text{-}CAR\}(H_2O)_2](H_2O)_2$	0.72	250°C	21.38 (21.86)	34.92 (35.10)	2.84 (3.09)	9.22 (9.63)
$[Ni_2\{(3\text{-fsa})_2\text{-}CAR\}(H_2O)_2](H_2O)_3$	2.21	250°C	19.69 (19.91)	34.52 (34.61)	3.21 (3.39)	9.34 (9.50)
$[Co_2\{(3\text{-fsa})_2\text{-}CAR\}(H_2O)_3]$	4.89	250°C	21.02 (21.25)	36.68 (36.83)	2.71 (2.88)	9.89 (10.11)
$[Cu_2\{(3\text{-fsa})_2\text{-}CAR\}](H_2O)_2$	1.91	250°C	13.01 (13.14)	42.09 (42.18)	3.68 (3.72)	11.29 (11.58)
$[Ni\{(3\text{-fsa})_2\text{-}CAR\}](H_2O)$	—	250°C	12.74 (12.74)	44.17 (44.28)	2.87 (3.03)	11.77 (12.16)
$[Cu_2\{(3\text{-fsa})_2\text{-}CAR\}(H_2O)]$	1.94	250°C	12.59 (12.77)	44.11 (44.26)	2.92 (3.03)	11.96 (12.15)

TABLE-3
(FUNGITOXICITY OF THE COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES AGAINST THE FUNGAL PATHOGENS *HELMINTHOSPORIUM ORYZAE* AND *FUSARIUM OXYSPORIUM*

Complexes	*Helminthosporium oryzae* % of inhibition over control					*Fusarium oxysporium* % of inhibition over control				
	100	200	400	800	1000	100	200	400	800	1000
Mononuclear copper(II)	12.2	18.8	24.5	59.4	68.9	11.9	17.2	23.3	54.2	65.2
Mononuclear nickel(II)	9.4	12.5	16.8	30.5	51.6	7.9	11.4	15.9	28.5	49.9
Mononuclear cobalt(II)	10.2	14.7	21.4	38.9	49.3	12.4	16.4	25.1	42.2	54.1
Dinuclear copper(II)	18.5	25.3	32.8	64.4	76.2	16.2	24.1	31.4	63.1	74.8
Dinuclear nickel(II)	13.2	15.7	19.3	33.1	56.6	15.1	18.2	21.5	41.2	62.1
Dinuclear cobalt(II)	14.3	18.9	24.4	41.5	59.1	12.2	16.6	22.7	39.1	57.0

Transition metal salts in the form of chlorides, sulphates and nitrates can not be used as fungicides, as they cause damage to the leaves[33]. However, when applied as coordination compounds they do little damage. Among the complexes reported here the copper(II) complexes exhibit maximum fungitoxicity. Between the two series, mono and dinuclear, the dinuclear complexes exhibit more fungitoxicity than the corresponding mononuclear complexes. This is quite obvious because of the higher concentrations of the metal ions in the dinuclear complexes.

The fungitoxicity of the dinuclear copper(II) complex is comparable to the commercial fungicide *Blitox.*

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REFRENCES

1. M. Tanaka, H. Okawa, T. Tamura and S. Kida, *Bull. Chem. Soc. Jpn.*, **47**, 1669 (1974).
2. H. Okawa, Y. Nishida, M. Tanaka and S. Kida, *Bull. Chem. Soc. Jpn.*, **50**, 127 (1977).
3. N. Torrihara, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, **51**, 3226 (1978).
4. K.C. Satpathy, A.K. Panda, R. Mishra and (Miss) I. Panda, *Acta Chim. Hung.*, **125**, 527 (1988).
5. K.C. Satpathy, A.K. Panda, R. Mishra and I. Panda and A.P. Chopdar, *Trans. Met. Chem.*, **14**, 381 (1989).
6. K.C. Satpathy, A.K. Panda, R. Mishra and I. Panda, *Trans. Met. Chem.*, **16**, 410 (1991).
7. K.C. Satpathy, A.K. Panda, R. Mishra, A. Mahapatra and A. Patel, *Synth. React. Inorg. Met-Org. Chem.*, **22**, 201 (1992).
8. K.C. Satpathy, A.K. Panda, A. Mahapatra and R. Mishra, *Synth. React. Inorg. Met-Org. Chem.* (in press).
9. N.A. Bailey, D.E. Fenton, R. Moody, C.D.R. deBarbarin, I.N. Sciambarella, J.M. Latner, D. Limosin and V. Mckee, *J. Chem. Soc. Dalton Trans.*, 2519 (1987).
10. M. Mashima, *Bull. Chem. Soc. Jpn.*, **35**, 1882 (1962).
11. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 3rd Ed. (1966).
12. M. Tanaka, K. Kitaoka, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, **50**, 2470 (1976).
13. (a) S.D. Robinson and M.F. Uttlly, *J. Chem. Soc.*, 1912 (1973).
    (b) H. Okawa, Y. Nishida, M. Tanaka and S. Kida, *Bull. Chem. Soc. Jpn.*, **50**, 126 (1977).
14. K. Nakamat,: Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1963).
15. I. Gama, *Bull. Chem. Soc. Jpn.*, **34**, 760 (1961).
16. Ref. No. 4.
17. R.C. Mishra, B.K. Mahapatra and D. Panda, *J. Indian. Chem. Soc.*, **58**, 80 (1983).
18. K.C. Satpathy, A.K. Panda, R. Mishra and A. Mahapatra, *Synth. React. Inorg. Met-Org. Chem.*, **19**, 29 (1989).
19. A.V. Nikolaev, V.A. Lagvienko and I.I. Myachina, Thermal Analysis, Academic Press, New York, Vol. 2, p. 779 (1969).
20. P.R. Shukla, V.K. Singh and J. Bhargava, *J. Indian. Chem. Soc.*, **59**, 620 (1982).
21. B. Singh, P.L. Maurya, B.V. Agrawala and A.K. Dey, *J. Indian. Chem. Soc.*, **59**, 620 (1982).
22. R.H. Holm, *J. Am. Chem. Soc.*, **82**, 5682 (1960).
23. M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc.*, **4**, 2411 (1970).

24. C. Busetto, F. Cariati, F. Fantucci, D. Galizzoli and F. Morazzoni, *J. Chem. Soc., Dalton Trans.*, 1712 (1973).
25. M.A. Hitchman, *Inorg. Chem.* **16**, 1985 (1977).
26. A.T. Casey and S. Mitra, Theory and Application of Molecular Paramagnetism, in E.A. Boudreaux and I.N. Mulay (Ed.), John Willy and Sons, New York, pp. 214, 221, 223 (1976).
27. J.C. Duff and E.J. Bills, *J. Chem. Soc.*, 1987 (1982).
28. J.C. Bailar (Jr) (Eds.), Inorganic Synthesis, McGraw-Hill Inc., New York, Vol. IV, p. 32 (1953).
29. B.A. Goodman and J.B. Raynar, *Topics in Inorganic Radiochemistry*, **13**, 316 (1970).
30. ________, *Topics in Inorganic Radiochemistry*, **13**, 375 (1970).
31. R.L. Dutta and A. Syamal, Elements of Magneto-Chemistry, S. Chand, New Delhi, p. 182 (1982).
32. J.G. Horsfall, *Bot. Rev.*, **11**, 357 (1945).
33. J.C. Bailar. H.J. Emeleus, R. Nyholm and A.F. Trotman, Comprehensive Inorganic Chemistry, Dickenson, p. 3 (1983).

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Contact Address:

PROFESSOR D. MEYERSTEIN
Department of Chemistry
Ben-Gurion University of the Negev
P.O.B. 653, Beer-Sheva-84105
ISRAEL

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Contact address:

PROFESSOR W.N. SPECKAMP
University of Amsterdam, Laboratory of Organic Chemistry
Nieuwe Achtegracht 129, 1018 WS Amsterdam
NETHERLANDS