Asian Journal of Chemistry Vol. 13, No. 3 (2001), 1168–1174

Preparation and Characterisation of Transition Metal Complexes of 4-Oximino-1-(2′,4′-dinitrophenyl)-3-Methyl-2-Pyrazolin-5-One

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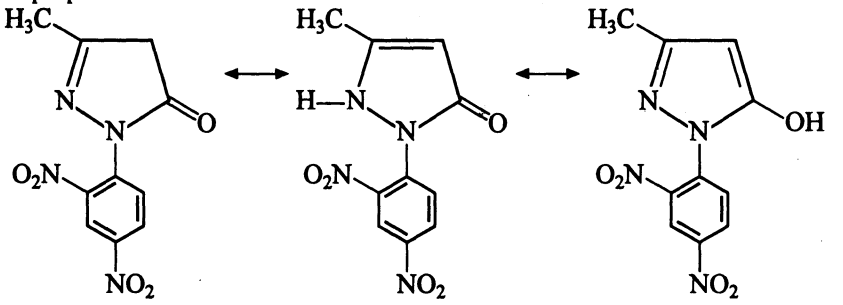
Oxovanadium(IV), chromium(III), managanese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 4-oximino-1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5-one have been prepared and characterized on the basis of elemental analysis, conductivity, magnetic moment and spectral studies. All complexes except chromium(III) and iron(III) having general composition $M(ODMPZ)_2 \cdot 2H_2O$ whill the chromium(III) and iron(III) complexes are $M(ODMPZ)_3$. The ligand field parameters for VO(II), Cr(III), Ni(II) and Co(II) chelates are also calculated.

INTRODUCTION

Nitrogen heterocyclic compounds have gained importance on account of their varied type of biological activities[1,2]. 1-(2′,4′-Dinitrophenyl)-3-methyl-2-pyrazolin-5-one [DMPZ] has been synthesized by a large number of workers[3–5] and proposed different tautomers of it[5,6].



CH : Form NH : Form OH : Form

[DMPZ]

1-[2′,4′-Dinitropnenyl]-3-methyl-2-pyrazolin-5-one is biologically important due to its tendency to exist in various tautomeric forms. A literature survey reveals that no work has been carried out on metal complexes derived from 4-oximino-1-(2′,4′-dinitropnenyl)-3-methyl-2-pyrazolin-5-one [ODMPZ]. There is much controversy in the m.p. and method of preparation of 1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5-one[3–5]. Controversy in m.p. may be due to a tendency to

form different tautomers by 1-(2′,4′-dinitropnenyl)-3-methyl-2-pyrazolin-5-one and also due to different solvents used for crystallization[3–5]. In the present communication we have adopted Chao's[4] method to prepare 1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5-one.

EXPERIMENTAL

All chemicals used were of reagent grade (BDH). 1-(2′,4′-Dinitrophenyl)-3-methyl-2-pyrazolin-5-one was synthesized (m.p. 92°C) by the reported method[4]. Its oxime (m.p. 245°C) was prepared by allowing a solution containing 2 parts of sodium nitrite to gradually and with shaking into cold hydrochloric acid solution containing 5-parts of 1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5-one. A yellow oil is separated which by addition of ether is made crystalline. The oxime was recrystallized from hot dioxane.

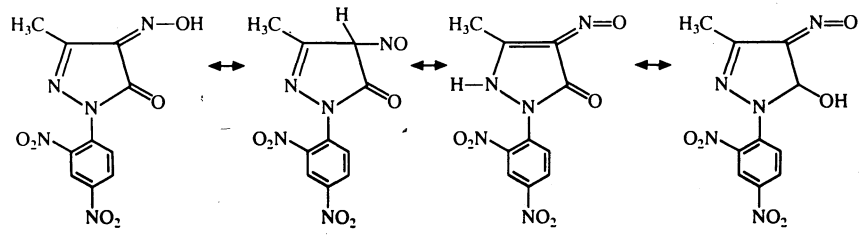
In the preparation of metal complexes of Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Mn(II), metal acetates were used. $VOSO_4 \cdot H_2O$ and $FeCl_3$ (anhydrous) were used in the preparation of VO(II) and Fe(III) complexes respectively. For the preparation of metal complexes the following general procedure was used. Metal salts were dissolved in hot distilled water. Hot ligand solution (in dioxane) in slight excess over the metal ligand (ratio 1 : 2) was added to it dropwise and with constant stirring. The resulting solution was refluxed for 2 h. The complex was formed immediately after addition of 2 g of sodium acetate. The metal complex was filtered and washed well with hot water and then with hot ethanol and dried in air.

Metals were estimated by standard gravimetric and volumetric method[7]. The elemental analysis, FT-IR spectra (in KBr), electronic spectra (in DMF) [CDRI, Lucknow], molar conductivity [EQUIP-TRONICS EQ-660], magnetic moment at room temperature [S.P. University, Vidyanagar] are recorded in Table-1.

RESULTS AND DISCUSSION

The elemental analysis (Table-1) reveals 1 : 3 (metal : ligand) stoichiometry for Cr(III) and Fe(III) complexes and 1 : 2 (metal : ligand) stoichiometry for all other metal complexes. The conductance measurement values [3.89–13.63 ohm^{-1} cm^2 $mole^{-1}$ in methanol] show that all metal complexes are non-electrolytes.

The possible resonance structures of 4-oximino-1-(2′,4′-dinitrophenyl)-3-methyl-2-pyrazolin-5-one [ODMPZ] ligand studied in the present work are:



(i) (ii) (iii) (iv)

[ODMPZ]

TABLE-1
ANALYTICAL, CONDUCTANCE AND MAGNETIC MOMENT DATA OF METAL COMPLEXES

Compound (Colour)	% Analysis, found (calcd.)				λ_m (ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff} (B.M.)
	M	C	H	N		
ODMPZ (Yellow)	–	41.48 (40.95)	2.47 (2.38)	22.99 (23.89)	–	–
$VO(ODMPZ)_2$ (Brown)	7.17 (7.82)	36.46 (36.86)	2.02 (1.84)	21.05 (21.50)	5.24	1.78
$Cr(ODMPZ)_3$ (Brown)	5.56 (5.60)	38.09 (38.79)	2.07 (1.94)	22.70 (22.63)	3.92	3.60
$Mn(ODMPZ)_2(H_2O)_2$ (Greenish yellow)	7.94 (8.13)	35.09 (35.56)	2.74 (2.37)	20.80 (20.74)	13.50	5.74
$Fe(ODMPZ)_3$ (Brown)	5.89 (5.99)	38.43 (38.63)	2.45 (2.25)	22.13 (22.53)	3.89	6.15
$Co(ODMPZ)_2(H_2O)_2$ (Dark brown)	8.74 (8.68)	35.54 (35.34)	2.54 (2.36)	20.70 (20.62)	3.28	4.34
$Ni(ODMPZ)_2(H_2O)_2$ (Green)	8.23 (8.65)	35.40 (35.36)	2.16 (2.36)	20.43 (20.63)	13.63	2.89
$Cu(ODMPZ)_2(H_2O)_2$ (Dark brown)	9.76 (9.29)	35.01 (35.11)	2.01 (1.85)	20.92 (20.48)	6.69	1.79
$Zn(ODMPZ)_2(H_2O)_2$ (Yellow)	9.89 (9.54)	35.45 (35.01)	2.40 (2,33)	20.50 (20.14)	4.24	–

The carbonyl oxime type of the ligand possesses five potential coordination sites; they are (1) and (2) ring nitrogens, (3) cyclic carbonyl oxygen, (4) nitrogen of —C=N (oxime) group, (5) oxygen of =N—OH group. The possibility of ring nitrogen (1) coordination to the metal ion is ruled out by zwitter ion mechanism[8,9]. The infrared spectra of ODMPZ showed a broad band *ca.* 3382 cm^{-1}, which may be due to ν(O—H) of oximino group[10–12]. On complexation, this band vanishes suggesting that the hydroxy group of oximino group is coordinated to the metal ion *via* deprotonation. The free ν(O—H) is generally found[13] between 3650–3500 cm^{-1}, similar to that of alcoholic ν(O—H). The ν(O—H) of several oximes involving intramolecular or intermolecular hydrogen bonding is remarkably lower and is dependent on the strength of the hydrogen bond formed in the oxime molecule[14]. The observed low value of ν(O—H) suggests the presence of intramolecular or intermolecular hydrogen bonding in ligand ODMPZ. These observations suggest that ligand ODMPZ in the present study may have tautomeric form (I). The ligand ODMPZ exhibits a medium band at *ca.* 3100 cm^{-1}, which may be assigned to overtone of ν(C=N) of oximino group[15].

The spectral data of ODMPZ as well as its metal complexes have certain features in the region 1700–900 cm^{-1} in their characterisation.

Infrared spectra of ODMPZ studied in the present work show a strong band at *ca.* 1736 cm^{-1}, may be due to ν(C=O) (ring)[15], which undergoes a low energy shift in all metal complexes and appears at 1732–1724 cm^{-1}. This indicates the coordination of cyclic carbonyl oxygen of ODMPZ to the metal ion.

Two bands of nearly equal intensity are observed in the region 1618–1590 cm^{-1} in the infrared spectrum of ODMPZ, which may be due to cyclic and oximino ν(C=N)[16]. The first band at 1590 cm^{-1} may be assigned to ν(C=N) (Cyclic)[8, 15], while the band at 1618 cm^{-1} may be assigned to ν(C=N) (oxime)[16]. The ν(C=N) (cyclic) of ODMPZ remains almost unchanged in the metal complexes, suggesting that ligand ODMPZ may have tautomeric form-I at least in the solid state and this observation also suggests that ring nitrogen-2 is not involved in the coordination. The ν(C=N) (oxime) of ODMPZ at *ca.* 1618 cm^{-1} undergoes a low energy shift by 4–7 cm^{-1} in all metal complexes. This may be due to coordinate bond formation through the nitrogen of oximino group[15].

The N—O stretching band observed in the IR spectra of ODMPZ at *ca.* 1024 cm^{-1} is shifted to higher wave number in all metal complexes. This observation suggests involvement of oximino group in the complex formation[17, 18].

The presence of strong and broad bands at 3425–3408 cm^{-1} in the IR spectra of metal complexes suggests the presence of coordinated water[15] molecule. The appearance of band in 865–835 cm^{-1} region is assigned to wagging modes of water molecule in Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)[19].

The strong band at *ca.* 864 cm^{-1} in the VO(II) complex may be assigned to ν(V=O) (associated)[20].

$$\ldots V{=}O \ldots V{=}O \ldots V{=}O \ldots V{=}O \ldots$$

The infrared spectra of all metal complexes show band at 543–505 cm^{-1} and at 465–408 cm^{-1}, which may be due to ν(M—O) and ν(M—N) modes respectively[19]. The infrared spectra of ligand and all metal complexes show strong band at *ca.* 1336 cm^{-1} may be due to $\nu(NO_2)$.[21]

The electronic spectra of all metal complexes are recorded in DMF.

The electronic spectra of $VO(ODMPZ)_2$ complex shows weak band at 11,415 cm^{-1}, 19,305 cm^{-1} and 26,559 cm^{-1} which are assigned to $b_2 \rightarrow e$ $\{-3DS + 5Dt\}$, $b_2 \rightarrow b_1$ $\{10Dq\}$ and $b_2 \rightarrow a$ $\{10Dq - 4Ds - 5Dt\}$ transitions respectively. Making[22] the use of the transition energies, Dt = 680 cm^{-1} has been evaluated, which measures the degree of tetragonality present in the field. In the tetragonal complex $b_2 \rightarrow b_1$ the transition is predicted to be equal to $10Dq^{xy}$ and hence[23] $Dq^z = 742$ cm^{-1} can be evaluated[23].

The parameter D_s, D_t and D_q have been used to calculate the absolute ligand field parameters[24] $D_T = 9213$ cm^{-1}, $D_Q = 42{,}164$ cm^{-1}, $D_S = 18{,}704$ cm^{-1}, $D_Q^{XY} = 53{,}065$ cm^{-1} and $D_Q^Z = 20{,}360$ cm^{-1}. D_Q is average ligand field experienced

by the central metal ion. $D_T/D_Q = 0.2185$ measures the degree of distortion. The value of D_Q^{XY} and D_Q^Z suggests that the field along XY plane is much stronger compared to that along Z-axis. The room temperature magnetic moment 1.78 B.M. is the range of octahedral to VO(II) complex.

The electronic spectrum of Cr(III) shows bands at 19,685 cm^{-1}, 20,202 cm^{-1} and at 26,666 cm^{-1} which may be assigned to $^4B_{1g} \rightarrow {}^4E_g$, $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4E_g$, A_{2g} transition respectively[25]. An attempt has been made to calculate Dt = 59 cm^{-1}, $Dq^{XY} = 2020$ cm^{-1} and $Dq^Z = 1916$ cm^{-1} using reported method[26, 28]. The absolute ligand field parameters DQ = 54,594 cm^{-1}, DT = 801 cm^{-1}, $DQ^{XY} = 55,540$ cm^{-1} and $DQ^Z = 52,702$ cm^{-1} have been evaluated[24, 27]. The value of ratio DT/DQ = 0.01467 suggests that $Cr(ODMPZ)_3$ is moderately distorted octahedral.[29] The room temperature magnetic moment for Cr(III) complexes is 3.60 B.M. The low μ_{eff} for complex may be due to positive spin-orbit coupling and small magnetic anisotropy irrespective of nature of band involved[30].

The electronic spectra of $Mn(ODMPZ)_2 \cdot (H_2O)_2$ shows band at 18,382 cm^{-1} and 25,687 cm^{-1} which may be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g respectively in an octahedral field[31]. The magnetic moment of the Mn(II) chelate is in the range required for octahedral structure[31].

The electronic spectra of $Fe(ODMPZ)_3$ shows bands at 18,234 cm^{-1}, 19,305 cm^{-1} and 26,115 cm^{-1} which may be assigned to transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g respectivley[32, 33]. The magnetic moment of Fe(III) chelate is higher than the required range of octahedral structure.

The electronic spectrum of high spin octahedral Co(II) chelate shows band at *ca.* 9259 cm^{-1} and *ca.* 19,120 cm^{-1}. The former band may be due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$ and the latter band may be due to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions[34]. The $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ transition is two electron transition and thus is expected to be much weaker. In the present study ν_2 transition remains almost unobserved. ν_2 transition (*ca.* 19,639 cm^{-1}) was calculated by band fitting procedure[35]. The observed transition energies were used to calculate 10 Dq ≃ 10,383 cm^{-1}, B = 732 cm^{-1}, $\beta = 0.7569$ cm^{-1}. The ν_2(calcd.)/$\nu_1 = 2.12$ ratio also suggests octahedral geometry for the chelate[35]. The magnetic moment of the Co(II) chelate is 4.34 B.M., slightly less than the required value for octahedral complexes[36].

The electronic spectrum of Ni(II) chelate shows[37] $\nu_1 : {}^3A_{2g} \rightarrow {}^3T_{2g}$ bands at 8665 cm^{-1} and 8850 cm^{-1}, $\nu_2 : {}^3A_{2g} \rightarrow {}^3T_{1g}$ bands at 18903 cm^{-1} and 20747 cm^{-1} and $\nu_3 : {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ band at 26596 cm^{-1}.

The ν_1 and ν_2 band of Ni(II) chelate is broad unsymmetrical weak band. It shows splitting into two components. The splitting of ν_1 and ν_2 band suggests the presence of tetragonal distortion[25] in the Ni(II) chelate. The lowering in symmetry is not reflected in ν_3 band. The $\nu_2/\nu_1 = 2.39$ is greater than the range required for

an octahedral structure[36]. The splitting energy of ν_1 and ν_2 bands can be used to calculate[25, 38] Dt = 22 cm^{-1}, Ds = 935 cm^{-1}, Dq^{XY} = 866 cm^{-1}, Dq^{Z} = 829 cm^{-1}. An attempt has also been made to calculate DT = 287 cm^{-1}, DS = 6546 cm^{-1}, DQ^{XY} = 23471 cm^{-1}, DQ^{Z} = 23255 cm^{-1} and DT/DQ = 0.122. The ratio DT/DQ provides a measure of tetragonal distortion. The room temperature magnetic moment for Ni(II) chelate is 2.89 B.M. in the range required for an octahedral structure[39, 40].

The electronic spectrum of Cu(II) chelate shows shoulder at 14,939 cm^{-1} and band at 17,123 cm^{-1}, which presumbly contains d-d transition[41]. Absence of any absorption below 10,000 cm^{-1} ruled out the possibility of tetrahedral structure for chelate[42]. The former band may be due to $^2B_{1g} \rightarrow {}^4A_{1g}(\nu_1)$ and the latter may be due to $^2B_{1g} \rightarrow {}^2B_{2g}(\nu_2)$ transitions for octahedral structure[43, 44]. The $^2B_{1g} \rightarrow {}^2E_g(\nu_3)$ transition remained unresolved in the Cu(II) chelate. A more intense band at *ca.* 23,866 cm^{-1} and *ca.* 26,410 cm^{-1} might be charge transfer in origin. An approximate value of 10 Dq = 8,952 cm^{-1} has been obtained from the splitting energies[41, 44]. The magnetic moment for Cu(II) chelate corresponds to one unpaired electron[45]

ACKNOWLEDGEMENTS

Financial assistance from Gujarat Government, Gandhinagar is gratefully acknowledged. The authors are thankful to Dahod Anaj Mahajan Sarvajanik Education Society, Prof. Y.K. Agrawal, Prof. J.R. Shah, Prof. H.C. Trivedi, Principal Dr. C.G. Dave and Principal Dr. A.M. Pancholi for the generous help during the research.

REFERENCES

1. J. Elguero, C. Marzin, A.R. Katritzky and P. Kinda, The Tautomerism of Heterocycles, Academic Press, New York (1976).
2. R.W. Taft, F. Anvia, M. Taageperaj, J. Catalan and J. Elguero, *J. Am. Chem. Soc.*, **108,** 3237 (1986).
3. Khromov-N.V. Borisov, *Chem. Abstr.*, **49,** 8257 (1955).
4. Z. Chao, *Chem. Abstr.*, **59,** 2795 (1963).
5. Johnston, *Chem. Abstr.*, **29,** 8003 (1935).
6. J. Elguero, Comprehensive Heterocyclic Chemistry, Pergamon Press, Oxford, Vol. 5, p. 167 (1984); Vol. 3, p. 1 (1996).
7. A.I. Vogel, A Text Book of Quantiatitive Inorganic Analysis, ELBS, London, 4th Edn., (1978).
8. R.C. Maurya, D.D. Mishra, S. Mukherjee, P.K. Trivedi and S.K. Jaiswal, *Synth. React. Inorg. Met-Org. Chem.*, **23,** 723 (1993).
9. R.C. Maurya and R. Verma, *J. Indian Chem. Soc.*, **75,** 29 (1998).
10. J. Sharma, Y. Singh and A.K. Rai, *Indian J. Chem.*, **36A,** 717 (1997).
11. A. Nigam, P. Sharma and Ashok Kumar, *Indian J. Chem.*, **36B,** 445 (1997).
12. A. Palm and H. Werbin, *Can. J. Chem.*, **32,** 858 (1954).

13. L. Birladeany, I.R. Spectra of Organic Compounds, Wiley, New York, p. 333 (1972).
14. R. Blink and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).
15. N.R. Shah and J.R. Shah, *J. Indian Chem. Soc.*, **58,** 851 (1981).
16. (a) K. Nakamoto, Infrared Spectra of Inorg. and Coordination Compounds, Wiley, New York (1963); (b) K. Nakamoto and P.J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, John Wiley & Sons, London (1968).
17. K.K. Ramaswamy, C.I. Jose and D.M. Sen, *Indian J. Chem.*, **5,** 156 (1967).
18. P.W. Sadler, *J. Chem. Soc.*, 2162 (1961).
19. M. Jayramundu and K.H. Reddy, *Indian J. Chem.*, **38A,** 1173 (1999).
20. (a) D.M.L. Goodgame and S.V. Waggett, *Inorg. Chim. Acta*, **5,** 155 (1971); (b) R.L. Farmer and F.L. Urback, *Inorg. Chem.*, **13,** 587 (1974).
21. T.N. Srivastava and J.D. Singh, *Indian J. Chem.*, **28A,** 422 (1989).
22. (a) J. Selbin, *Coord. Chem. Rev.*, **1,** 293 (1966); (b) J. Selbin and T.R. Ortolano, *J. Inorg. Nucl. Chem.*, **26,** 37 (1964).
23. M.P. Teotia, J.N. Gurtu and V.B. Rana, *Indian J. Chem.*, **19A,** 133 (1980).
24. J.C. Donini, B.R. Hollebone, G. London, A.B.P. Lever and J.C. Hempel, *Inorg. Chem.*, **14,** 455 (1975).
25. A.B.P. Lever, *Coord. Chem. Rev.*, **3,** 119 (1968).
26. R.A.D. Wentworth and T.S. Piper, *Inorg. Chem.*, **4,** 709 (1965).
27. J.C. Donini, B.R. Hollebone and A.B.P. Lever, *Prog. Inorg. Chem.*, **22,** 225 (1977).
28. J.R. Perumareddi, *Coord. Chem. Rev.*, **4,** 73 (1969).
29. M.P. Teotia, J.N. Gurtu and V.B. Rana, *J. Inorg. Nucl. Chem.*, **42,** 821 (1980).
30. B.C. Guha, *Proc. Royal Soc.*, **A-206,** 353 (1951).
31. L.S. Sankhla and S.N. Mishra, *J. Indian Chem. Soc.*, **57,** 300 (1980).
32. A.K. Srivastava, V.B. Rana and Modan Mohan, *J. Inorg. Nucl. Chem.*, **36,** 3864 (1974).
33. A. Sreekantan and C.C. Patel, *Proc. Indian Acad Sci.*, **87A,** 455 (1978).
34. B. Singh, Lakshmi and U. Agrawal, *Inorg. Chem.*, **8,** 2341 (1969).
35. N.A. Patel, R.P. Patel and J.R. Shah, *Indian J. Chem.*, **19A,** 236 (1980).
36. D.K. Rastogi and K.C. Sharma, *J. Inorg. Nucl. Chem.*, **36,** 2219 (1974).
37. E. Konig and K. Madeja, *Inorg. Chem.*, **6,** 48 (1957).
38. D.K. Rastogi and K.C. Sharma, *J. Inorg. Nucl. Chem.*, **36,** 2219 (1974).
39. A. Earnshaw, B.N. Figgis, J. Lewis and R.D. Peacock, *J. Chem. Soc.*, 3132 (1961).
40. A. Anagnostopoulous, *J. Inorg. Nucl. Chem.*, **35,** 3366 (1973).
41. A.K. Srivastava, A.L. Varshney and P.C. Jain, *J. Inorg. Nucl. Chem.*, **42,** 47 (1980).
42. L.W. Laue and L.T. Taylor, *J. Coord. Chem.*, **2,** 295 (1973).
43. L.F. Larkworthy and K.C. Patel, *J. Inorg. Nucl. Chem.*, **32,** 1264 (1970).
44. D.E. Billing and A.E. Underhill, *J. Inorg Nucl. Chem.*, **30,** 2147 (1968).
45. A. Syamal and K.S. Kale, *Indian J. Chem.*, **19A,** 225 (1980).

(*Received:* 21 March 2001; *Accepted:* 4 May 2001) AJC-2337