Asian Journal of Chemistry Vol. 20, No. 1 (2008), 521-529

Synthesis and Spectroscopic Characterization of Palladium(II) and Platinum(II) Complexes with Substituted Pyrazoles

NIMAIRATAN ADHIKARI* and NITYANANDA SAHA (DECEASED)†
Department of Chemistry, A.P.C. College, New Barrackpore
24 Parganas (N), Kolkata-700 131, India
Fax: (91)(33)25378797; E-mail: adhikari.nr@gmail.com

Pd(II) and Pt(II) complexes with substituted pyrazoles (**1a-d**) with various counter ions, X (X = Cl^-, Br^-, NO_3^-, SCN^- and ClO_4^-) have been synthesised and characterized. Magnetic and electronic spectral data classify all the non-electrolyte mono-chelates as square planar species. IR data (down to 200 cm^{-1}) point out that the two acid ligands (**1a** and **1b**) and ester ligand (**1c**) exhibit neutral bidentate (NN) through two tertiary N atoms however the hydrazide one (**1d**) exercises neutral bidentate (NO) through pyrazolyl 2_N and amidic oxygen, respectively. The counter ions are coordinated. A noticeable downfield shift of all most all of the protons in ^1H NMR spectra has been immense helpful regarding binding sites.

Key Words: Synthesis, Spectroscopy, Monochelate, Palladium(II), Platinum(II).

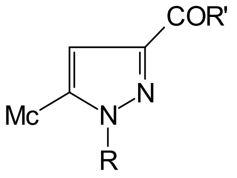
INTRODUCTION

The anticancer activity of *cis*-dichloro diammine platinum(II)[1-4], commonly known as '*cis*-platin' or *cis*-DDP has initiated tremendous global interest in studies relating to the design, synthesis and characterization of related complexes which could mimic the interactions of metal ions with DNA. In line with the first suggestion of Furst[5], group VIIIB metals, in general, have been included in recent years in the design of model metallic species with the expectation of having remarkable potentiality as anticancer drugs[6]. A fair number *cis*-Pt(II) complexes with N-donor ligands containing labile anions have been well known for their cytostatic activities[7,8]. As reported by Williams *et al.*[9], the introduction of Pd(II) in search of anticancer materials is based on the fact that Pd(II) complexes are more reactive than those of Pt(II) and rapid ligand exchage can occur. Kirschner *et al.*[10] noted that *cis*-dichloropiperidine Pd(II) can induce filamental growth in *E. coli*. The same authors reported in a separate communication[11], that some Pd(II) complexes with S and N donor ligands exhibit potential antitumour activity. Complexes of other metal ions, particularly those Ni(II),

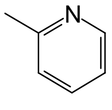
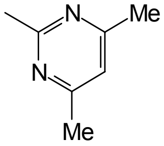
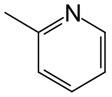
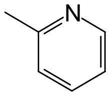
---

†Department of Chemistry, University of Kalyani, Kalyani-741 235, India.

Zn(II), Pd(II), Rh(III) and Ru(III), in this field, show promising activity with less toxic effects, sometimes even superior to the well-known Pt(II) species[12]. In view of the above information and in continuation of earlier work[13-16], the present communication reports the synthesis and spectroscopic (electronic, vibrational and ^1H NMR) characterization of Pd(II) and Pt(II) complexes using substituted pyrazoles[1-3] having general structural formulation as **I** as given in the following:



1

	R	R′	Ligand	
1a		OH	PyPzCH	5-Methyl-1-(2´-pyridyl)-pyrazole-3-carboxylic acid
1b		OH	PymPzCH	5-Methyl-1-(4´,6´-dimethyl-2´-pyrimidyl)-pyrazole-3-carboxylic acid
1c		OEt	EMPyPzC	Ethyl-5-methyl-1-(2´-pyridyl)-pyrazole-3-carboxylate
1d		$NHNH_2$	MpyPzCH	5-Methyl-1-(2´-pyridyl)-pyrazole-3-carbohydrazide

EXPERIMENTAL

All the materials used at different stages for the preparation of the ligands and complexes were analR grade quality and were used without further purification. Spectrograde solvents were used for spectral and conductance measurements. DMSO-d_6 (Aldrich) was used for recording ^1H NMR data.

C, H and N analyses were carried out with a Perkin-Elmer CHNS/O analyzer 2400 at IACS(Cal). ^1H NMR spectra of some of the species together with their ligands were recorded in DMSO-d_6 with Bruker AM 300 L (300 MHz) super-conducting FT NMR. Palladium content in the complxes was determined gravimetrically as palladium(II) dimethylglyoximate after decomposing the complex, in each case,with an acid mixture (*viz.*, conc. HNO_3 + HCl) and platinum content in the complexes was determined as metallic platinum by standard procedure. The halogen content of the complexes was determined as silver halide following the standard procedure. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer at IACS, Calcutta. The molar conductance values of the complexes in DMF solution were obtained with a Systronics model 304 digital conductivity meter. The diffused reflectance spectra and the solution spectra in DMF of the complexes were recorded on U-3501 spectrophotometer. IR spectra were recorded on a Perkin-Elmer model 883 infrared spectrophotometer in the solid state (KBr pellet).

Preparation of K_2PdCl_4: An aqueous solution (10 mL) of KCl (148 g, 2 mmol) was added to an aqueous suspension of $PdCl_2$ (0.177g, 1 mmol suspended in 20 mL H_2O) at water bath temperature. The resultant solution was filtered off and the filtrate (taking on a porcelain basin) was evaporated to dryness. The mass was dried in a $CaCl_2$ desiccator at room temperature (301 K) and collected.

Preparation of K_2PtCl_4 from K_2PtCl_6: To an aqueous solution (20 mL) of K_2PtCl_6 (1.0 g, 2 mmol) placed water bath was added dropwise an aqueous solution (10 mL) of $NH_2NH_2·H_2O$ (0.05 g, 1 mmol) with vigorous stirring under controlled condition and addition was stopped when Pt-black in very small quantity appeared. The red-brown solution was filtered off and the filtrate was evaporated to dryness on water bath temperature. The residual mass was dried in a $CaCl_2$ desiccator at room temperature (301 K) and collected.

Synthesis of ligands: The ligands (**1a-d**) were synthesised and characterized as earlier reported methods[1-3].

Synthesis of metal ion complexes

$PdLCl_2$ (L = 1a-d): An aqueous ethanolic solution (20 mL) of K_2PdCl_4 (2 mmol) was added to an aqueous ethanolic solution (20 mL) of the ligands (2 mmol) with stirring at water bath temperature; reddish brown to yellow colour developed at the recorded pH *ca.* 3-4. The resultant solution was then concentrated to a small bulk (*ca.* 10 mL) at water bath temperature and cooled down to room temperature; whereby the respective complex separated out. It was filtered off, washed with aqueous ethanol and dried in a $CaCl_2$ desiccator at room temperature (301 K) and collected.

$PdLX_2$ (L = 1a-d, X = Br, NO_3, SCN, ClO_4): An aqueous suspension of $PdLCl_2$ (L = **1a-d**) (1 mmol in 20 mL H_2O) was treated with two molar proportions of NH_4X (2 mmol) and refluxed for 1 h at water bath temperature when the expected ‘metathesis’ reaction occurred. The resulting solutions of varying colours (brown to yellow) were cooled down to room temperature and the precipitated complex species were filtered off, in each case and dried in the usual manner.

$PtLCl_2$ (L = 1a,1b,1d): An aqueous ethanolic solution (20 mL) of K_2PtCl_4 (0.2 g, 0.5 mmol) was added to an aqueous ethanolic solution (10 mL) of the ligands (0.5 mmol) stirring with a glass rod; whereby an yellow colour of varying intensities developed at the recorded pH *ca.* 3-4.

The resultant solution was concentrated at water bath temperature and then cooled to room temperature. The respective compound separated out. It was filtered off, washed with ethanol and dried in $CaCl_2$ desiccator.

RESULTS AND DISCUSSION

A fair number of novel Pd(II) and Pt(II) complexes of the above ligands (L) were prepared in aqueous ethanol and through metathesis reaction procedure which are solid, air stable and coloured (Table-1). The sequential routes of the synthesis may be given as follows:

$K_2PdCl_4 + L \rightarrow PdLCl_2$ (in aq. ethanol medium and pH *ca.* 3-4)
$PdLCl_2 + 2NH_4X \rightarrow PdLX_2$ (metathesis reaction; refluxed for 1 h)
($X = Br, NO_3, SCN, ClO_4$; L = **1a-d**)
$K_2PtCl_4 + L \rightarrow PtLCl_2$ (aq. ethanol; L = **1a, 1b, 1d**)

These complex species conform to the general composition, MLX_2 (M = Pd(II), L = **1a-d**; X = Cl, Br, NO_3, SCN, ClO_4; M = Pt(II), L = **1a, 1b, 1d**; X = Cl) as ascertained from elemental analysis. All these species are non-electrolytes (Λ_M = 8-30 mho cm^2 mol^{-1}) (Table-1) and uniformly diamagnetic in nature as expected for a d^8 ion in a square-planar geometry. It has been reported by earlier workers[17-19] that the electronic spectra of square-planar complexes of Pd(II) and Pt(II) are extremely difficult for assignment to proper transitions, since the electronic energy levels vary according to the nature of the ligand. In the present study, the diffuse reflectance spectra of the present species show in general, a broad band appearing in the region 20,100-27,800 cm^{-1} which can be assigned as a first approximation, to the spin-allowed *d-d* transition of $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1B_{1g}$ and $^1E_{1g}$ type[18] in square-planar geometry. All these species are fairly soluble in DMF giving yellow to brown solution of varying intensity. The electronic spectra of such solutions show broad band in general, around in the region 26,300-37,200 cm^{-1} associated with high molar extinction coefficient (ε *ca.* 10^3); this can be ascribed to MLCT bands coupled with possible inter/intra ligand transitions[19,20]. The electronic spectra of $[Pt(MPyPzCH)X_2]$ shows a broad band around 20,120 cm^{-1} associated with high molar extinction coefficient (ε *ca.* 10^3) indicates the mixing of *d-d* transition with CT band and assignment becomes difficult.

In IR spectra of MLX_2 [M = Pd(II)/Pt(II), L= **1a-c**], the asymmetric stretching vibration of the carbonyl function has been shifted ($\nu\Delta$ = 5-50 cm^{-1}) to the higher frequency region. The fact rules out the participation of carbonyl oxygen in complexation. However, a significant negative shift

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF Pd(II) AND Pt(II) COMPLEXES

Complex (colour)	Yield (%)	Elemental analysis: Found/(Calcd.) %					Λ_M (**)	μ_{eff} at 301 K (BM)
		C	H	N	M	Anion		
[Pd(PyPzCH)Cl_2]	90	31.7	2.4	11.2	28.2	18.8	10	Dia
Brownish yellow		(31.5)	(2.3)	(11.0)	(28.0)	(18.6)		
[Pd(PyPzCH)Br_2]	85	25.8	2.0	8.9	22.6	34.3	12	Dia
Creamy yellow		(25.5)	(1.9)	(8.9)	(22.7)	(34.0)		
[Pd(PyPzCH)$(NO_3)_2$]	85	27.9	2.0	146.1	24.2	–	10	Dia
Grey		(27.6)	(2.1)	(16.1)*	(24.6)			
[Pd(PyPzCH)$(SCN)_2$]	75	28.4	2.2	16.2	25.0	–	10	Dia
Brown		(28.1)	(2.1)	(16.4)*	(25.1)			
[Pd(PyPzCH)$(ClO_4)_2$]	70	23.4	1.8	8.1	21.3	–	12	Dia
Creamy yellow		(23.6)	(1.7)	(8.2)	(20.9)			
[Pt(PyPzCH)Cl_2]	80	25.7	1.8	8.7	41.2	15.3	20	Dia
Pale brown		(25.5)	(1.9)	(8.9)	(41.6)	(15.1)		
[Pd(PymPzCH)Cl_2]	85	32.5	3.0	13.4	26.2	17.6	8	Dia
Straw yellow		(32.2)	(2.9)	(13.6)	(26.0)	(17.3)		
[Pd(PymPzCH)Br_2]	80	26.7	2.4	11.0	21.4	32.4	10	Dia
Dark brown		(26.4)	(2.4)	(11.2)	(21.4)	(32.0)		
[Pd(PymPzCH)$(NO_3)_2$]	80	28.6	2.5	18.0	23.1	–	10	Dia
Brown		(28.5)	(2.6)	(18.1)*	(23.0)			
[Pd(PymPzCH)$(SCN)_2$]	85	29.2	2.6	18.2	23.2	–	10	Dia
Yellowish brown		(29.0)	(2.5)	(18.4)*	(23.4)			
[Pd(PymPzCH)$(ClO_4)_2$]	70	24.3	2.3	10.2	19.6	–	16	Dia
Yellowish brown		(24.4)	(2.2)	(10.4)	(19.8)			
[Pt(PymPzCH)Cl_2]	80	45.7	3.1	19.1*	10.0	–	12	Dia
Creamy yellow		(45.5)	(3.1)	(19.3)	(10.1)			
[Pd(EMPyPzC)Cl_2]	85	35.5	3.3	10.1	26.3	17.8	10	Dia
Brownish yellow		(35.2)	(3.1)	(10.3)	(26.1)	(17.4)		
[Pd(EMPyPzC)Br_2]	90	28.7	2.5	8.2	21.2		10	Dia
Bright brown		(28.9)	(2.6)	(8.4)	(21.4)	–		
[Pd(EMPyPzC)$(NO_3)_2$]	80	31.5	2.9	15.0	23.2		12	Dia
Pale brown		(31.2)	(2.8)	(15.7)*	(23.1)	–		
[Pd(MPyPzCH)Cl_2]	95	30.6	2.8	17.5	27.1		20	Dia
Greenish brown		(30.4)	(2.7)	(17.7)	(27.7)	18.3		
[Pd(MPyPzCH)Br_2]	80	24.9	2.2	14.2	22.1	(17.9)	10	Dia
Pale brown		(24.8)	(2.3)	(14.5)*	(22.0)	33.3		
[Pd(MPyPzCH)$(NO_3)_2$]	90	26.6	2.6	21.7	23.9	(33.0)	10	Dia
Pale brown		(26.8)	(2.4)	(21.9)	(23.8)	–		
[Pd(MPyPzCH)$(SCN)_2$]	75	27.5	2.5	22.1	24.3		20	Dia
Brownish yellow		(27.2)	(2.5)	(22.3)	(24.2)	–		
[Pt(MPyPzCH)Cl_2]	80	24.6	2.4	14.2	40.2		20	Dia
Yellow		(24.8)	(2.2)	(14.5)	(40.4)	–		

*Including nitrogen present in the anion; **Molar conductance in DMF (mho cm^2 mol^{-1})

($\nu\Delta$ = 10-50 cm^{-1}) in the stretching frequency of the carbonyl function is found when L = **1d**. This suggests the involvement[21] of the carbonyl oxygen (neutral) in complexation. In the ir spectra of the present Pd(II)/Pt(II) complexes under studies, the ν(C=N) (pyridyl/pyrimidyl) vibrations have been found to experience definite positive shifts ($\nu\Delta$ = 5-25 cm^{-1}) [with the exception that in the mono-chelates of Pd(II)/Pt(II) with **1d** suffers a negative shift; $\nu\Delta$ = 5-30 cm^{-1}]. These results point out the participation[13-16] of tertiary N atoms (pyrazolyl 2_N and pyridyl/pyrimidyl $1'_N$) in the mono-chelates when L = **1a-c** and only pyrazolyl 2_N when L = **1d**. Similar positive shifts have been found for transition metal ion complexes of other N-heterocyclic bases[22]. Far IR data down to 200 cm^{-1} further support the earlier propositions as following: the appearance of new non-ligand bands in the regions 400-380, 310-280 and 265-245 cm^{-1} may be safely assigned to ν(M-O) (carbonyl, neutral)[23], ν(M-N) (pyrazole)[15] and ν(M-N) (pyridyl/pyrimidyl)[15], respectively.

Chloro complexes: IR spectra of MLX_2 (M = Pd(II)/Pt(II); L = **1a-d**; X = Cl) the two diagnostic IR band frequencies ν(M-Cl) are observed around 380-320 cm^{-1} which suggest that two chloride ions are coordinated to the central Pd(II) or Pt(II) ion in *cis* position[23].

Bromo-complexes: MLX_2 (M = Pd(II); L = **1a-d**; X = Br). The characteristic band frequencies due to ν(M-Br) are observed in the IR spectra around 330-340 cm^{-1} indicating coordinated nature of bromide ion[26].

Thiocyanate-complexes: MLX_2 (M = Pd(II); L= **1a, 1b, 1d**; X = SCN). The IR spectra show a strong sharp band around 2110-2175 cm^{-1} in all its species and another sharp band at 1960 cm^{-1} is found when L = **1b**. These are attributed to ν(C=N) stretch of thiocyanate group[27,28]. The ν(C-S) stretching band is located near 765-720 cm^{-1} indicating that the S end of the ambidentate thiocyanate group is bonded to the central metal ions[29,30].

Nitrato-complexes: MLX_2 (M = Pd(II); L = **1a-d**; X = NO_3). The spectra show three bands in the region 1425-1385, 1330-1300 and 835-800 cm^{-1}: the first two bands can be assigned to the components of ν_3 and the last one to the ν_2 vibration of a monodentate-nitrate group in C_{2V} symmetry[31].

Perchlorato complexes: MLX_2 (M = Pd(II); L = **1a, 1b**; X = ClO_4). The characteristic IR frequencies due to perchlorate group appear around 1195-1120, 1140-1070 and 1050-1040 cm^{-1}, respectively which could be assigned to the split components of ν(Cl-O) stretching frequency of monodentate perchlorate group in a C_{3V} symmetry[32].

A scrutiny of the available ^{1}H NMR spectral data in the light of a comparative study between the free ligand molecules and of their representative Pd(II)/Pt(II) complexes reveal that there is an appreciable down field shift (Table-2) of all most all the protons present in the ligand

TABLE-2

^{1}H NMR CHEMICAL SHIFTS OF SOME Pd(II) AND Pt(II) COMPLEXES COMPARED WITH THEIR LIGANDS

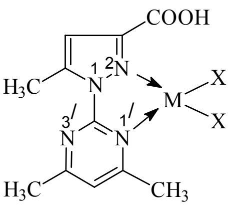
δ in ppm

Compound	4-H	5-CH_3	3-COOH	3´-H	4´-H	5´-H	6´-H	4´-CH_3	6´-CH_3	-CH_2-	-CH_3-	-NH-	-NH_2
PyPzCH	6.69	2.56	11.93	7.83	8.01	7.43	8.50	–	–	–	–	–	–
[Pd(PyPzCH)Cl_2]	6.68	2.56	–	7.82	8.01	7.44	8.51	–	–	–	–	–	–
[Pd(PyPzCH)$(SCN)_2$]	6.68	2.56	–	7.82	8.01	7.44	8.51	–	–	–	–	–	–
[Pt(PyPzCH)Cl_2]	6.68	2.69	11.22	8.31	8.58	7.58	9.18	–	–	–	–	–	–
PymPzCH	6.67	2.53	–	–	–	7.32	–	2.47	2.47	–	–	–	–
[Pd(PymPzCH)Cl_2]	6.72	2.52	–	–	–	7.45	–	2.45	2.45	–	–	–	–
[Pd(PymPzCH)$(SCN)_2$]	6.86	2.52	–	–	–	7.46	–	2.46	2.68	–	–	–	–
[Pt(PymPzCH)Cl_2]	6.67	2.52	–	–	–	7.31	–	2.48	2.48	–	–	–	–
EMPyPZC	6.74	2.56	–	7.82	8.01	7.43	8.50	–	–	4.26	1.26	–	–
[Pd(EMPyPZC)Cl_2]	6.74	2.58	–	8.43	8.25	7.64	8.92	–	–	4.39	1.29	–	–
[Pd(EMPyPZC)Br_2]	6.74	2.58	–	7.96	8.07	7.67	8.82	–	–	4.24	1.23	–	–
MPyPZCH	6.61	2.56	–	7.92	7.99	7.37	8.46	–	–	–	–	9.50	4.39
[Pd(MPyPZCH)Cl_2]	6.71	2.82	–	8.16	8.49	7.42	8.93	–	–	–	–	10.29	–

molecules complexed with Pd(II)/Pt(II) metal ions. The fact can be well explained as due to the electrical field effect. It has been observed that in ^{1}H NMR spectrum of [Pd(PymPzCH)$(SCN)_2$], the three methyl protons at 6′-CH_3 suffer maximum down field shift (Table-2) and this can be attributed as probably owing to its position closest to pyrimidyl nitrogen which is a possible bonding site. The proton at 6′-H in the pyridine ring of the corresponding ligand molecules complexed with Pd(II)/Pt(II) suffers definitely downfield shift (Table-2); the fact can be explained as 6′-H, closest to pyridyl $1'_N$ (a possible binding site) experiences a definite electrical field effect in the metal complexes. In the ^{1}H NMR spectrum of [Pd (MPyPzCH)Cl_2], the amide proton (-NH) closest to the carbonyl function, resonates at high δ values supporting the carbonyl O as donor site in the said species. Thus ^{1}H NMR spectra have been immense helpful for the bonding characteristics of the concerned ligand molecules in Pd(II)/Pt(II) species and are in close agreement with observations based on IR data.

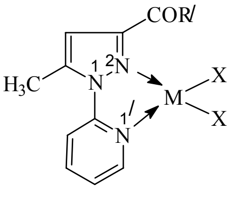
Conclusion

The metal-ligand framework of the novel species under study can be best described in the follwing structures (**I, II, III**) drawn on the basis of spectral and physicochemical measurements as follows:



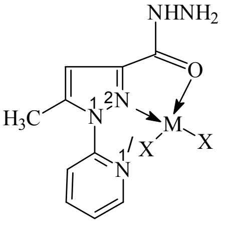
I

M = Pd(II), X = Cl, Br, NO_3, SCN, ClO_4
M = Pt(II), X = Cl
R′ = OEt, M = Pd(II), X = Cl, Br, NO_3



II

R′ = OH, M = Pd(II), X = Cl, Br, NO_3, SCN, ClO_4,
R′ = OH, M = Pt(II), X = Cl



III

M = Pt(II), X = Cl
M = Pd(II), X = Cl, Br, NO_3, SCN

ACKNOWLEDGEMENTS

The author (NA) is grateful to UGC, New Delhi, India for financial support to the Minor Research Project [No.F. PSW-020/05-06 (ERO)]. Thanks are also due to Prof. S.K. Kar, Calcutta University for various helps and discussions. The author expresses the sincere gratitude to the Principal and colleagues, Department of Chemistry, A.P.C. College, 24 Parganas (N), India for their constant encouragement.

REFERENCES

1. N. Adhikari and N. Saha, *J. Indian Chem. Soc.*, **83**, 427 (2006).
2. N. Adhikari and N. Saha, *J. Chem. Sci.* (Communicated).
3. N. Adhikari and N. Saha, *J. Chem. Res.*, 645 (2006).
4. B. Rosenberg, *Platinum Met. Rev.*, **15**, 42 (1971).
5. A. Furst, in ed.: Kugeluass, Chemistry of Chelation in Cancer, American Lectures in Living Chemistry Series, Springfield ILL (1963).
6. M.J. Cleare, *Coord. Chem. Rev.*, **12**, 349 (1974).
7. A. Khan, *J. Clin. Hematol. Oncol.*, **7**, 1 (1977).
8. B. Rosenberg, *Biochimic*, **60**, 859 (1978).
9. R.D. Graham and D.R. Williams, *J. Inorg. Nucl. Chem.*, **41**, 1245 (1979).
10. S. Kirschner, A. Maurer and C. Dragulesku, *J. Clin. Hematol. Oncol.*, **7**, 293 (1977).
11. Kirschner, A. Maurer and C. Dragulesku, *J. Clin. Hematol. Oncol.*, **7**, 190 (1977).
12. M. Das and S.E. Livingstone, *Br. J. Cancer.*, **37**, 466 (1978).
13. N. Saha, D. Mukherjee and S.K. Kar, *Inorg. Chim. Acta*, **67**, 137 (1982).
14. N. Saha, D. Bhattacharyya and D. Mukherjee, *Inorg. Chim. Acta*, **125**, 213 (1986).
15. N. Saha and D. Mukherjee, *Inorg. Chim. Acta*, **137**, 161 (1987).
16. N. Saha, A. Saha and A. Mishra, *Polyhedron*, **13**, 2025 (1994).
17. H.B. Gray and C.J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).
18. C.J. Ballhausen, N. Bjerum and R. Dinge, *Inorg. Chem.*, **4**, 514 (1965).
19. H. Basch and H.B. Gray, *Inorg. Chem.*, **6**, 365 (1967).
20. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsivier, p. 354 (1968).
21. S. Trofimenko, *Chem. Rev.*, **72**, 502 (1972).
22. J.P. Ferraro, *Appl. Spectros.*, **23**, 160 (1969).
23. J.H. Groen, J.G.P. Delis, P.W.N.M. van Leeuwen and K.Vrieze, *Organometallics*, **16**, 68 (1997).
24. W. Levason and McAuliffe, *Inorg. Chim. Acta*, **16**, 167 (1976).
25. J. Dehand and J. Jordanov, *Inorg. Chim. Acta*, **17**, 40 (1976).
26. R.J. Dosser and A.E. Underhill, *J. Inorg. Nucl. Chem.*, **36**, 1239 (1974).
27. A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).
28. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, edn. 3, p. 270 (1977).
29. M.M. Chamberlain and J.C. Baillar Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1951).
30. J.L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).
31. N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
32. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(*Received*: 22 November 2006; *Accepted*: 14 September 2007) AJC-5854