Pergamon

PII: S0277–5387(98)00127–2

Polyhedron Vol. 17, No. 19, pp. 3439–3444, 1998
© 1998 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/98 $19.00 + 0.00

Complexes of hexadentate NSO donor ligands-III. Nickel(II) complexes of 1,3-di(*o*-salicylaldiminophenylthio)propane and 1,2-di(*o*-salicylaldiminophenylthio)xylene

Shefali Pal,[a] Saktiprosad Ghosh,[a]* Gurucharan Mukherjee[b] and Asok Kumar Nandi[c]

[a]Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 700 032, India

[b]Department of Chemistry, Presidency College, Calcutta, 700 073, India

[c]Central Glass and Ceramic Research Institute, Calcutta, 700 032, India

(Received 8 October 1997; accepted 27 March 1998)

Abstract—Nickel(II) complexes of the hexadentate $N_2S_2O_2$ donor ligands, 1,3-di(*o*-salicylaldiminophenylthio)propane (H_2DSALPTP) and 1,2-di(*o*-salicylaldiminophenylthio)xylene (H_2DSALPTX) have been synthesised and characterised. H_2DSALPTP reacted with $NiCl_2.6H_2O$ or $Ni(ClO_4)_2.6H_2O$ in presence of ammonia to give the complex [Ni(DSALPTP)] (**1**). H_2DSALPTX reacted smoothly with $Ni(ClO_4)_2$ to yield the corresponding complex [Ni(DSALPTX)] (**2**). The ligand did not react with $NiCl_2$ in the absence of ammonia but in its presence produced the complex (**2**). The molecular and crystal structure of [Ni(DSAL PTX)] exhibits a very unusual deployment of the six donor sites of the ligand. It crystallises in the orthorhombic system with space group $P2_12_12_1$. In dichloromethane solution both the complexes are found to exhibit Ni(II)/Ni(III) redox couples in their cyclic voltammograms at room temperature with $E_{1/2}$ values 0.87 and 0.78 V (vs. Ag/AgCl).

Keywords: hexadentate NSO-donors; Ni(II) complexes; X-ray and molecular structure; electrochemical studies.

Hexacoordinating flexidentate ligands with ONS donor sites in strategic positions of the donor framework are not commonly encountered in coordination chemistry and our group has explored some of them previously [1, 2]. Disclosure of the fact that nickel is an essential constituent of several hydrogenases [3] and that nickel sites are believed to have a distorted octahedral arrangement consisting of 2 or 3 sulphur atoms and the rest nitrogen and/or oxygen atoms [4, 5] prompted us to undertake the study of nickel complexes of the ligands which have $N_2S_2O_2$ donor sites. Nickel bound to sulphur and nitrogen/oxygen is also present in carbon monoxide dehydrogenases [6]. The catalytic properties of hydrogenase arise from the remarkably low oxidation potential for the nickel(II)/nickel(III) redox couple [3b,7]. In this paper we report the synthesis, characterisation and cyclic voltammetric studies of the nickel(II) complexes of two $N_2S_2O_2$ donor ligands. The molecular structure of [Ni(DSALPTX)] is also reported and it reveals a very large distortion of the coordination environment around the nickel(II) acceptor centre from the perfect octahedron.

EXPERIMENTAL

Synthesis of the ligands

They were prepared by methods described earlier [1].

---

* Author to whom correspondence should be addressed.

Synthesis of the complexes

[Ni(DSALPTP)](**1**): A solution of $NiCl_2.6H_2O$ (0.24 g, 1 mmol) or $Ni(ClO_4)_2.6H_2O$ (0.33 g, 1 mmol) in methanol (20 cm^3) was added to a stirring solution of the ligand (0.49 g, 1 mmol) in chloroform (20 cm^3) and the mixture was stirred for 1 h. A few drops of 6(N) NH_3 was then added to the mixture. The mixture was further stirred for 48 h. Red precipitate separated out which was recrystallised from methanol (yields: 75%).

[Ni(DSALPTX)] (**2**): This complex was prepared by the same procedure as above by taking $NiCl_2.6H_2O$ (0.24 g, 1 mmol) as the starting metal salt and H_2DSALPTX (0.56 g, 1 mmol) as the ligand, with a few drops of 6(N) NH_3. The complex was recrystallised from methanol with an yield of about 70%. $Ni(ClO_4)_2.6H_2O$ readily reacts with the ligand in the same ratio in absence of NH_3 to give the same orange-red product. It was recrystallised from methanol (yield 75%).

Physical measurements

Physical measurements were done as reported in our earlier communications [1, 2]. Electrochemical data were collected with a BAS CV-27 and a BAS model X-Y recorder at 298 K. The electrodes used were flat platinum disc working electrode, Pt wire auxiliary electrode and a Ag/AgCl reference electrode.

Crystal structure determination of [*Ni*(*DSALPTX*)] (*2*)

X-ray data were collected in Enraf-Nonius-CAD-4 diffractometer for a crystal mounted on top of a glass fibre. The unit cell parameters were determined from a least-square refinement of 17 high angle reflections. The three intensity controlled reflections (-3 1-2, 3-1-2, -4-3-4) checked every hour, showed no significant variations (±0.5%). The intensities were corrected for Lorentz-polarisation effects and an empirical absorption correction was also made [8]. A total of 3250 unique reflections measured contained 3118 with $F_o \geqslant 4\sigma(F_o)$. The structure was solved by direct methods using the program, SHELXS-86 [9] which revealed the positions of all the non-hydrogen atoms. The program SHELXL-93 [10] was used to refine the structure. Refinement on F using anisotropic displacement parameters for all non-hydrogen atoms was performed. Positions of 11 hydrogen atoms were located from the difference Fourier map. The other 14 residual hydrogen atoms were placed in their calculated positions with a temperature factor 1.2 times the U_{eq}. of the parent atom to which it is attached. Coordinates of the 11 hydrogen atoms and their isotropic temperature factors were refined. Figure 1 shows thermal ellipsoid of the molecule, excluding the hydrogen atoms for the clarity of the figure. The final full matrix least-square refinement coverged at R to 0.053. Crystallographic data and additional details regarding data collected and refinement are given in Table 1.

Structure description

The compound [Ni(DSALPTX)] crystallises in the $P2_12_12_1$ space group with four molecules in general position. The ligand binds the Ni(II) acceptor centre in a distorted octahedral pattern. The square base of the octahedron is defined by the O(A), S(B), S(A) and O(B) atoms with two nitrogen N(A) and N(B) in the two apical positions. Selected bond lengths and bond angles are given in Table 2 and a few selected torsion angles are listed in Table 3. The two phenolate oxygen and thioether sulphur donors occupy cis-positions of the distorted square plane defined by O(A)–O(B)–S(A) and S(B) with the Ni(II) ion centrally placed on it with a mean deviation of −0.012(2)A. The bite

Table 1. Crystal data and structure refinement for [Ni(DSALPTX)] (**2**)

Identification code	(**2**)
Empirical formula	$C_{34}H_{26}N_2NiO_2S_2$
Formula weight	617.40
Temperature	293(2) K
Wavelength	1.54187 A
Crystal system	Orthorhombic
Space group	P_{212121}
Unit cell dimensions	$a = 13.0850(10)$ Å
	$\alpha = 90^\circ$
	$b = 14.1150(10)$ Å
	$\beta = 90^\circ$
	$c = 15.252(3)$ Å
	$\gamma = 90^\circ$
Volume	2817.0(6) $Å^3$
Z	4
Density (calculated)	1.456 gm/cm^3
Absorption coefficient	2.659 mm^{-1}
$F(000)$	1280
Crystal size	0.20 × 0.20 × 0.25 mm
Theta range for data collection	4.27 to 74.91°
Index ranges	$0 \leqslant h \leqslant 16, 0 \leqslant k \leqslant 17, 0 \leqslant l \leqslant 19$
Reflections collected	3250
Unique reflections	3250
$F_o \geqslant 4\sigma(F_o)$	3118
Refinement method	Full-matrix least-squares on F
Data/restraints/parameters	3250/0/415
Goodness-of-fit on F_o	0.292
Final R indices $[F_o > 2\sigma(F_o)]$	$R = 0.0527$
R indices (all data)	$R = 0.0543$
Extinction coefficient	0.0018(3)
Largest diff. peak and hole	1.023 and −0.699 e. $Å^{-3}$

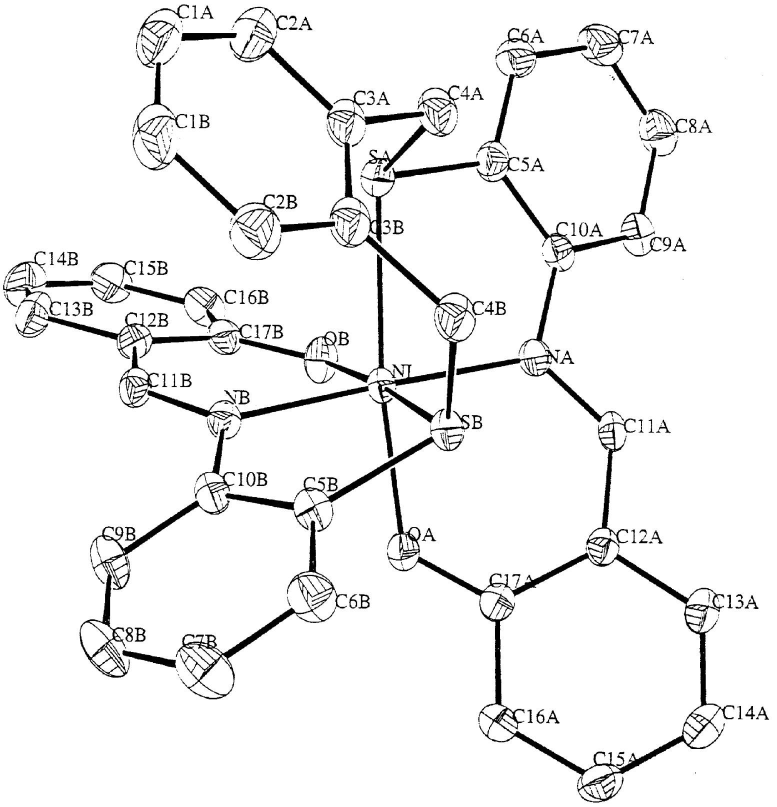

Fig. 1. The thermal ellipsoid of [Ni(DSALPTX)] excluding the hydrogen atoms.

angles involving the two sulphur atoms S(A) and S(B) generates highly distorted seven membered ring Ni–S(B)–C(4B)–C(3B)–C(3A)–C(4A)–S(A). Each bite angle corresponding to a pair of nitrogen and oxygen donors attached to the Ni(II) centre is found to form two six membered rings (Ni–O–C(17)–C(12)–C(11)–N) and the N–S donor pairs to create two five membered chelate rings (Ni–S–C(5)–C(10)–N). The bite angle corresponding to the pair S(A)–Ni–S(B), O(A)–Ni–O(B) are 96.99(5)° and 96.7(2)° respectively and for the other other pair O(A)–Ni–S(B) and O(B)–Ni–S(A) are 81.97(13)° and 84.90(14)° respectively. The severe distortion of the coordination octahedron being clearly manifested in the values of the angles at the metal centre generated by the six donor points. The observed bond distances (vide Table 2) fall well within the range found in most of the distorted octahedral Ni(II) complexes accommodating thioether sulphur coordination [11]. The large distortion of the coordination octahedron is probably arising due to the unusual orientation of the donor sites of the ligand which is very difficult to anticipate and is a clear indication of the flexidentate nature of the ligand.

No hydrogen bonding or any intermolecular short contacts are observed in the lattice. The molecules are packed in the lattice by intermolecular van der Waals forces. Each five-membered and six-membered chelate ring formed with the Ni(II) ion is also attached with a benzene ring and the dihedral angles of each chelate ring with its corresponding benzene ring lie in the range of 6–16°.

RESULTS AND DISCUSSION

The complexes synthesised and characterised during the present investigation are [Ni(DSALPTP)] (**1**) and [Ni(DSALPTX)] (**2**) in which both the ligands function as dibasic hexadentate donors. The ligand H_2DSALPTP did not react at all with either $NiCl_2$ or $Ni(ClO_4)_2$ in the absence of ammonia, but H_2DSALPTX is found to react with $Ni(ClO_4)_2$ in absence of NH_3 to produce a yellowish-green compound. On recrystallisation from methanol it yielded the orange-red compound (**2**). However, H_2DSALPTX does not react with $NiCl_2$ without the presence of ammonia. When, however, the ligand is reacted with $Ni(ClO_4)_2$ in presence of ammonia, a different compound separated out which was identified as $[Ni(DAPTX)(NH_3)](ClO_4)_2$, H_2DAPTX being the diamine dithioether ligand 1,2-di(*o*-aminophenylthio)xylene whose Pd(II), Ni(II) and Cu(II) compounds were reported earlier [12, 13]. It is quite probable that base hydrolysis of the Schiff base generated the ligand *in situ* which then coordinated to the Ni(II) ion. Single crystals for X-ray diffraction

Table 2. Selected bond lengths [Å] and angles [°] for [Ni(DSALPTX)]

Bond lengths (Å) and angles (°) involving Ni atom			
Ni–O(B)	1.988(4)	Ni–N(A)	2.045(5)
Ni–O(A)	1.995(4)	Ni–S(A)	2.448(2)
Ni–N(B)	2.032(4)	Ni–S(B)	2.476(2)
O(B)–Ni–O(A)	96.7(2)	N(B)–Ni–S(A)	98.24(14)
O(B)–Ni–N(B)	91.4(2)	N(A)–Ni–S(A)	83.57(13)
O(A)–Ni–N(B)	88.2(2)	O(B)–Ni–S(B)	174.51(12)
O(B)–Ni–N(A)	90.3(2)	O(A)–Ni–S(B)	81.97(13)
O(A)–Ni–N(A)	90.0(2)	N(B)–Ni–S(B)	83.24(13)
N(B)–Ni–N(A)	177.7(2)	N(A)–Ni–S(B)	95.08(13)
O(B)–Ni–S(A)	84.90(14)	S(A)–Ni–S(B)	96.99(5)
O(A)–Ni–S(A)	173.35(12)		
Bond lengths and angles in the five-membered ring			
S(A)–C(5A)	1.766(6)	S(B)–C(5B)	1.762(5)
C(5A)–C(10A)	1.413(8)	C(5B)–C(10B)	1.398(7)
N(A)–C(10A)	1.408(7)	N(B)–C(10B)	1.428(7)
C(7B)–C(8B)–C(9B)	121.8(6)	C(7A)–C(8A)–C(9A)	120.6(6)
C(5B)–C(10B)–N(B)	118.3(5)	C(5A)–C(10A)–N(A)	118.6(5)
C(10B)–N(B)–Ni	117.4(3)	C(10A)–N(A)–Ni	118.1(4)
C(5B)–S(B)–Ni	93.0(2)	C(5A)–S(A)–Ni	94.6(2)
Bond lengths and angles in the six-membered ring			
N(A)–C(11A)	1.297(7)	N(B)–C(11B)	1.292(7)
C(11A)–C(12A)	1.435(8)	C(11B)–C(12B)	1.434(8)
C(12A)–C(17A)	1.430(8)	C(12B)–C(17B)	1.410(8)
O(A)–C(17A)	1.284(6)	O(B)–C(17B)	1.292(7)
C(11A)–N(A)–Ni	122.0(4)	C(11B)–N(B)–Ni	122.4(4)
N(A)–C(11A)–C(12A)	126.7(5)	N(B)–C(11B)–C(12B)	127.4(5)
C(11A)–C(12A)–C(17A)	123.2(5)	C(17B)–C(12B)–C(11B)	123.2(5)
O(A)–C(17A)–C(12A)	124.4(5)	O(B)–C(17B)–C(12B)	125.7(5)
C(17A)–O(A)–Ni	124.3(3)	C(17B)–OB–Ni	125.5(4)
C(4A)–S(A)–Ni	113.7(2)		
Bond lengths and angles in the seven-membered ring			
S(A)–C(4A)	1.837(6)	C(4B)–S(B)–Ni	125.4(2)
C(3A)–C(3B)	1.400(10)	C(3B)–C(4B)–S(B)	116.1(4)
C(3A)–C(4A)	1.505(9)	C(3A)–C(3B)–C(4B)	122.3(6)
S(B)–C(4B)	1.827(6)	C(3B)–C(3A)–C(4A)	121.8(6)
C(3B)–C(4B)	1.513(8)	C(3A)–C(4A)–S(A)	108.8(4)

Table 3. Lists of selected torsion angles for [Ni(DSALPTX)]

Atoms defining the torsion angles	Angle (°)	Atoms defining the torsion angles	Angle (°)
N(B)–Ni–O(A)–C(17A)	−145.9(4)	N(B)–Ni–S(A)–C(5A)	−166.7(2)
N(A)–Ni–O(A)–C(17A)	32.7(4)	N(A)–Ni–S(A)–C(5A)	14.9(2)
O(B)–Ni–S(A)–C(5A)	−75.9(2)	O(B)–Ni–O(A)–C(17A)	122.9(4)
S(B)–Ni–S(A)–C(5A)	109.2(2)	S(B)–Ni–O(A)–C(17A)	−62.5(4)
O(A)–Ni–S(A)–C(5A)	28.7(2)		

were grown from methanol-ether solution. Two compounds were identified in the crop of crystals. One was the complex (2) and the other one was the Ni(II)-salicylaldehyde complex. This indicates that partial hydrolysis of the imine moiety occurred leading to the rupture of the Schiff base ligand to produce salicylaldehyde, which led to the formation of the Ni(II) salicylaldehyde complex.

Table 4. Analytical data[a], electrical conductivity[b], magnetic moments, infrared and electronic spectral[c] data for the complexes

	C	H	N	Ni	Λ_M (ohm^{-1} cm^2	μ_{eff}	ν(C=N)/	ν(Ni–S)	λ_{max}, cm^{-1}
Complex		(%)			mol^{-1})	(B.M.)	(cm^{-1})		(ϵ, dm^3 mol^{-1} cm^{-1})
[Ni(DSALPTP)] (**1**)	62.5 (62.7)	4.1 (4.3)	4.9 (5.05)	10.9 (10.6)	3.4	2.95	1605	305	17241(sh), 22727 (17,429), 34482 (24,645)
[Ni(DSAL PTX)] (**2**)	66.4 (66.2)	4.1 (4.2)	4.3 (4.5)	9.9 (9.5)	6.9	3.25	1590	360	17857(sh) 22988(1,794), 31250(38,277) 38461(14,738)

[a] Calculated values in parentheses.
[b] Measured in nitromethane.
[c] Measured in dichloromethane.

Infrared, electronic spectra, magnetic moment and conductance

In the IR spectra of the complex [Ni(DSALPTP)](**1**) and [Ni(DSALPTX)](**2**) the ν(O–H) band of the corresponding ligands observed at 3500 and 3400 cm^{-1} respectively are absent due to the coordination of the deprotonated phenolic –OH to the Ni(II) acceptor centre. The ν(C=N) bands of the ligands observed at 1610 and 1600 cm^{-1} respectively are red shifted by 5–10 cm^{-1} in the spectra of the complexes (**1**) and (**2**) pointing to the involvement of the azomethine nitrogen in coordination. In the complexes (**1**) and (**2**), bonding from the thioether sulphur is indicated by the 50–35 cm^{-1} red shift of the ν(–S–CH$_2$) mode of the ligands observed as split bands at 700 and 650 cm^{-1} for H$_2$DSALPTP and at 660 and 640 cm^{-1} for H$_2$DSALPTX. Bands observed below 400 cm^{-1} (Table 4) (which are absent in the spectra of the ligand) are attributed to Ni–S linkage. These observations are in complete agreement with X-ray crystallographic data. The electronic spectral data supports the octahedral stereochemistry of the complexes (vide Table 4). [Ni(DSAL PTP)] and [Ni(DSAL PTX)] both exhibit bands in the 17,000 cm^{-1} region. The expected lower energy band could not be detected as it is out of the range of the scanning instrument. The third *d-d* band expected in the higher energy region could not be identified due to the presence of intense charge-transfer bands in the UV region. Both the complexes exhibit normal room temperature magnetic moment values of 2.95–3.25 B.M. and both behave as non electrolytes in nitromethane solution. The findings corroborate that both the phenolic-OH are deprotonated during complexation, the ligands coordinating as their dianions DSALPTP^{-2} and DSAL PTX^{-2}.

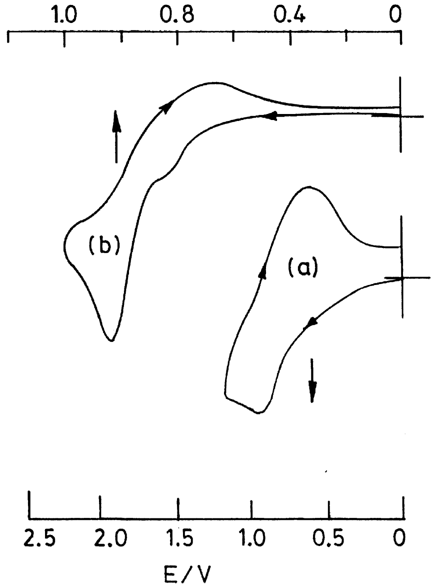

Fig. 2. Cyclic voltammograms of solutions of (a) [Ni(DSALPTP)] (scan rate 200 mvs^{-1}) and (b) [Ni(DSALPTX)](scan rate 50 mvs^{-1}) in dichloromethane using platinum electrode and NEt$_4$ClO$_4$ as supporting electrolyte.

Electrochemical studies

Cyclic voltammograms of [Ni(DSALPTP)] and [Ni(DSALPTX)] are shown in Fig. 2 with peak potentials listed in Table 5. Ni(II)-Ni(III) oxidation potential data in the case of thioether complexes generally lie in the range, 0.3–0.8 V [14]. The redox behaviour of the complexes have been examined in dichloromethane solution. The cyclic voltammogram of [Ni(DSALPTP)] exhibits a quasi-reversible Ni(II)/Ni(III) redox couple centered at 0.87 V vs. Ag/AgCl and that of [Ni(DSALPTX)] displays a reversible couple at 0.78 V. Therefore the E$_{1/2}$ values of these complexes lie at the higher end of the thioether contaning Ni(II) species indicating that Ni(II) is fairly stabilised in both the complexes. The ligand

Table 5. Electrochemical data[a]

Complex	$E_{1/2}$ (V)	ΔE_p (mV)[c]
[Ni(DSAL PTP)] (**1**)	0.87	300
[Ni(DSAL PTX)] (**2**)	0.78	120

[a] In CH_2Cl_2 (0.1 M TEAP) at a platinum electrode with an Ag/AgCl reference electrode.

[b] From cyclic voltammetry at a scan rate of 200 mVs^{-1}.

[c] Peak-to-peak separation.

H_2DSALPTP offers comparatively better stabilisation of the Ni(II) state towards oxidation. No cathodic responses was observed for both the complexes up to -1.5 V.

CONCLUSION

This work illustrates the coordination behaviour of two interesting hexadentate NSO donor ligands towards Ni(II). Structure of [Ni(DSALPTX)] exhibits the very unusual deployment of the six donor points of the ligand H_2DSALPTX while coordinating to the Ni(II) acceptor centre. Only single crystal X-ray diffraction study could establish such unusual orientation of the donor sites.

Acknowledgements—We are thankful to the National Diffractometer Facility (DST), Department of Biophysics, All India Institute of Medical Science, New Delhi for X-ray diffraction data collection. S. P. is grateful to C.S.I.R. for financial support in the form of a Research Associateship.

REFERENCES

1. Pal, S., Poddar, S. N. and Mukherjee, G., *Polyhedron*, 1993, **12,** 2465.
2. Pal, S., Poddar, S. N., Ghosh, S. and Mukherjee, G., *Polyhedron*, 1995, **14,** 3023.
3. (a) Thompson, A. J., *Nature*, 1982, **298**, 602; (b) Cammack, R., Lancaster, Jr., J. R. (ed.), *The Bioinorganic Chemistry of nickel*, VCH, New York, (1988), Chapter 8.
4. (a) Lindahl, P. A., Kojima, N., Hausinger, R. P., Fox, J. A., Teo, B. K., Walsh, C. T.and Orme-Johnson, W. H., *J. Am. Chem. Soc*., 1984, **106**, 3062. (b) Scott, R. A., Wallis, S. A., Czechowski, M., Vartannian, D. V. De, Gall, J Le, Peck, Jr., H. D. and Moura, I., *J. Am. Chem. Soc*., 1984, **106**, 3864.
5. (a) Teixeira, M., Moura, I., Xavier, A. V., Huynh, B. H., Vartannian, D. V. De, Peck, Jr., H. D., Gall, J. Le and Moura, J. J., *J. Biol Chem*., 1985, **260**, 8942. (b) Cammack, R., Patil, D., Hatchikian, E. C. and Fernandez, V. M., *Biochem. Biophys. Acta*, 1987, **912**, 98. (c) Teixeira, M., Moura, I., Xavier, A. V., Moura, J. J. G., Gall, J. Le, Vartannian, D. V. De, Peck, Jr., H. D. and Huynh, B. H., *J. Biol. Chem*., 1989, **264**, 16435.
6. Shukla, R., Mondal, S. and Bharadwaj, P. K., *Polyhedron*, 1993, **12,** 83 and references cited therein.
7. Cammack, R., *Adv. Inorg. Chem*., 1988, **32,** 297.
8. North, A. C., Philips, D. C. and Mathews, F. S., *Acta Crystallography*, 1968, **A24,** 351.
9. Sheldrick, G. M., *SHELXS* 86, A program for the solution of crystal structure. University of Gottingen, Germany, (1986).
10. Sheldrick, G. M., *SHELXL* 93, A program for the refinement of crystal structure. University of Gottingen, Germany, (1986).
11. Cooper, S. R., Rawle, S. C., Hartman, J. A. R., Hintsa, E. J. and Admans, G. A., *Inorg. Chem*., 1988, **27,** 1209.
12. Pal, S., Mukherjee, G. and Poddar, S. N., *Trans. Met. Chem*., 1994, **19,** 99.
13. Pal, S., Poddar, S. N. and Mukherjee, G., *Trans. Met. Chem*., 1994, **19,** 449.
14. Karmakar, S., Bhanjachoudhury, S., Ray, D. and Chakraborty, A., *Polyhedron*, 1993, **12,** 291.