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The chemistry of pyridine thiols and related ligands—8. Synthesis, NMR spectroscopy and crystal structure of first *trans*-[bis(pyridine-2-thiolato-S)-bis(triphenyl phosphine) platinum(II)]

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Abstract—Reaction of bis(pyridine-2-thiolato-N,S)platinum(II) (**1**) in acetonitrile (obtained from $PtCl_2$ and $Na^+C_5H_4NS^-$) with two equivalents of PPh_3 forms monomeric $Pt(C_5H_4NS)_2(PPh_3)_2$ (**2**) whose X-ray structure has been determined. It crystallises from a acetonitrile–chloroform mixture and exists as a centrosymmetric square planar monomer. Pyridine-2-thiolate binds to Pt via S-atoms in a *trans*-configuration and the other two positions are occupied by P atoms of PPh_3. The interatomic important parameters are: Pt–S = 2.343(2), Pt–P = 2.3147(13), C–S = 1.739(6) Å, bond angles P–Pt–P* and S–Pt–S* each = 180.0°, P–Pt–S, P*–Pt–S = 85.24° (acute) and P–Pt–S*, P*–Pt–S = 94.76° (obtuse). It represents the first example of a structurally characterised S-bonded pyridine-2-thiolato Pt(II) complex. The NMR data (^1H, ^{13}C, ^{31}P) suggest dissociation of **2** in $CDCl_3$ as follows: $Pt(C_5H_4NS)_2(PPh_3)_2$ (**2**)$\rightarrow$$Pt(C_5H_4NS)_2(PPh_3)$ (**2a**)$+PPh_3$. Both N,S- and S-bonded $C_5H_4NS^-$ moieties are confirmed from ^1H and ^{13}C NMR. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: triphenyl phosphine; pyridine-2-thione; biochemically active chromophores; S-bonded platinum(II) complex; pendant pyridyl.

INTRODUCTION

In recent years, there is an upsurge in coordination chemistry of heterocyclic thiones containing chemically active chromophores of the type: –N(H)–C(=S)↔–N=C(–SH), because these ligands provide several possibilities of metal–ligand interactions and have biochemical implications [1–4]. Pyridine-2-thione(C_5H_5NS), the simplest prototype of heterocyclic thiones binds to a metal center in several ways: S-bonding(η^1), S-bridging(η^2), N,S-chelating(η^2), N,S-bridging(η^2), N,S-chelating-cum-S-bridging(η^3) and N,S-bridging-cum-S-bridging(η^3) [4–13]. For structurally characterised Pt(II or III) complexes, N,S-bridging is observed in $[Pt_2(en)_2(\mu\text{-N,S-}C_5H_4NS)_2]Cl_2\cdot 3H_2O$ [14], $[Pt_2\{\mu\text{-N,S-}C_5H_3(4\text{-}CH_3)NS\}_2]$[15], $[Pt_2Cl_2(\mu\text{-N,S-}C_5H_4NS)_4]\cdot 2CHCl_3$ [15], and chelation in $[Pt(\eta^2\text{-N,S-}C_5H_4NS)(PPh_3)_2](PF_6)$ [16].

As a part of our interest in coordination chemistry of C_5H_5NS or its derivatives [17–19], we report the crystal structure of $[Pt(C_5H_4NS)_2(PPh_3)_2]$ (**2**) which represents the first example of a platinum(II) complex containing monodentate S-bonded $C_5H_4NS^-$ moiety. The solid state behaviour of **2** is compared with its solution phase behaviour. In literature [20], $C_5H_4NS^-$ ligand scrambling in $Pt(C_5H_4NS)_2(PPh_3)$ has been mentioned. In this investigation, we establish both N,S- and S-bonding modes for the species [**2a**, $Pt(\eta^2\text{-N,S–}C_5H_4NS)(\eta^1\text{-S–}C_5H_4NS)(PPh_3)$] in $CHCl_3$ using multinuclear NMR (^1H, ^{13}C and ^{31}P) spectroscopy and collecting massive scans for ^{13}C NMR spectrum.

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EXPERIMENTAL

General materials

Platinum(II) dichloride was procured from M/s Central Drug House Pvt (Bombay) while PPh_3 from Spectrochem. Pvt. (Bombay). 2-Hydroxypyridine was procured from M/s Sisco, Bombay. Pyridine-2-thione-(C_5H_5NS) was prepared as described previously [21, 22]. Sodium salt, $Na^+C_5H_4NS^-$ was prepared as described [17] for $Na^+C_5H_4NOS^-$. Acetonitrile was dried over P_2O_5 and other solvents dried by usual methods.

Preparation of $Pt(C_5H_4NS)_2$ (*1*) *and* $Pt(C_5H_4NS)_2(PPh_3)_2$ (*2*)

$Pt(C_5H_4NS)_2$ (**1**, yellow) was prepared from the stoichiometric reaction of $PtCl_2$ (0.186 g, 0.70 mmol) with C_5H_4NSNa (0.205 g, 1.54 mmol) in CH_3CN (25 cm^3) under reflux for *ca.* 20 h. The concentration of the solution under vacuum formed a yellow coloured solid which was treated with water to remove NaCl, recrystallised from CH_3CN and dried *in vacuo*. Yield, 40%, m.p. (°C) > 250, analytical data (%), found C, 30.4, H, 2.13, N, 6.95; required for $C_{10}H_8N_2S_2Pt$, C, 29.0, H, 1.93, N, 6.75, *IR* data (cm^{-1}), 1137s ($\nu C{=}S$), 426s (νPt–S), 254m (νPt–N).

$Pt(\eta^1\text{-}S\text{–}C_5H_4NS)_2(PPh_3)_2$ (**2**, yellow) was prepared by the addition of PPh_3 (0.160 g, 0.613 mmol) to $Pt(C_5H_4NS)_2$ (0.127 g, 0.306 mmol) in CH_3CN (20 cm^3) with magnetic stirring under reflux for 2 h. The excess solvent was removed under vacuum to get a yellow solid which was purified using diethylether and recrystallised from CH_3CN. Yield, 60%, m.p. (°C), 140–45, analytical data found (%), C, 58.2, H, 3.62, N, 3.02, required for $C_{46}H_{38}N_2P_2S_2$ Pt, C, 58.8, H, 4.04, N, 3.00, *IR data* (cm^{-1}), 1110s ($\nu C{=}S$), 430m (νPt–S).

Physical measurements

The elemental analysis for C, H and N were obtained using a Carlo-Erba 1108 microanalyser or from RSIC Chandigarh. The melting points were determined with a Gallenkamp electrically heated apparatus. The NMR spectra were recorded in $CDCl_3$ using, (i) Bruker AMX 300 spectrometer at 300.14 and 75.48 MHz probe frequencies for (^1H and ^{13}C resonances, respectively, with TMS as the internal reference) and (ii) Bruker AMX 500 spectrometer at 202.45 MHz probe frequency for $^{31}P\{^1H\}$ resonance with 85% H_3PO_4 as the external reference (δP, 27.5 ppm).

X-ray data collection and reduction

The crystal of $Pt(C_5H_4NS)_2(PPh_3)_2$ (**2**) was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least squares refinement of diffraction data from 25 reflections in the range of $10.60° < \theta < 18.04°$ in a ENRAF-NONIUS MACH3 automatic diffractometer [23]. Data were collected at 293 K using MoK radiation ($\lambda = 0.71073$ Å) and the ω scan technique and corrected for Lorentz and polarisation effects [24]. An empirical absorption correction was made [25]. A summary of crystal data, experimental details and refinement results are listed in Table 1.

Structure-solution and refinement

The structure was solved by direct methods [26] which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [27]. The hydrogen atoms were located in their calculated positions (C–H = 0.93–0.96 Å) and were refined using a riding model. After all shift/e.s.d ratios were less than 0.001, the refinement converged to the agreement factors listed in Table 1. The atomic scattering factors taken from International Tables for X-ray Crystallography [28] while molecular graphics were prepared using ZORTEP [29].

RESULTS AND DISCUSSION

Description of the crystal structure of $Pt(C_5H_4NS)_2(PPh_3)_2$ (*2*)

The selected interatomic parameters are given in Table 2 while Fig. 1 shows the molecular structure together with numbering scheme. The basic structural unit is a centrosymmetric monomer $Pt(C_5H_4NS)_2(PPh_3)_2$ (**2**). Two P atoms of PPh_3 molecules and two S atoms of $C_5H_4NS^-$ ligand coordinate to Pt atom in a square planar geometry with *trans* P–Pt–P* and S–Pt–S* angles of 180.0°, two acute (85.24°, P–Pt–S and P*–Pt–S*) and two obtuse (94.76°, P–Pt–S* and S–Pt–P*) angles. Chelation in *cis*-$[Pt(\eta^2\text{-}N,S\text{–}C_5H_4NS)(PPh_3)_2](PF_6)$ (**3**) causes more severe distortion as anticipated [e.g. *trans* S–Pt–P = 165.6°; N–Pt–P = 163.8(2)] [16]. It is significant that $C_5H_4NS^-$ can modulate the geometric positions of PPh_3 ligand as in **3** and **2** based on its coordination requirements. The Pt–P distance is normal but marginally longer than in **3** [Pt–P = 2.295, 2.253 Å] [16], while Pt–S distance [Pt–S = 2.348 Å] as well as P–C_{Ph} distance [1.832 Å] are nearly the same. The S–C(2) distance shows partial double bond character in the usual manner. The bite angle of S–C(2)–N(1) [120.7(5)°] is typical of monodentate $C_5H_4NS^-$ [117.6(7)°] as in $Hg(C_5H_4NS)_2$ [30] or is similar to the bridging $C_5H_4NS^-$ derivative [122–124°] in Pt(II) complexes [15]. Finally, the Pt–S–C(2) angle is also similar to the one in dimeric complexes [109.0(8)°]. **2** represents the first structurally characterised Pt(II) 3complex containing monodentate S-bonded $C_5H_4NS^-$ moiety. The steric effect due to

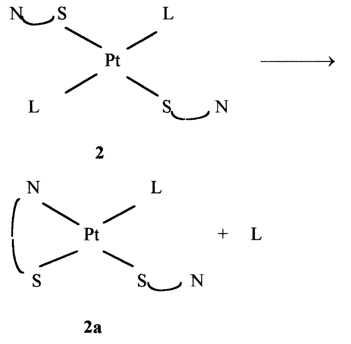
Table 1. Crystal data and structure refinement for [Pt(C_5H_4NS)$_2$ (PPh_3)$_2$]

Empirical formula	$C_{46}H_{38}N_2P_2PtS_2$
Formula weight	939.93
Crystal system/Space group	Monoclinic/$P2_1$/n
Unit cell dimensions	$a = 10.000(2)$ Å; $\alpha = 90.00(-)^\circ$ $b = 15.456(3)$ Å; $\beta = 97.04(2)^\circ$ $c = 12.989(2)$ Å; $\gamma = 90.00(-)^\circ$
Volume	1992.4(7) Å^3
Z	2
Density (calculated)	1.567 Mg/m^3
Absorption coefficient	3.742 mm^{-1}
F (000)	936
Crystal description	*yellow prism*
Crystal size	0.40 × 0.30 × 0.20 *mm*
No. of reflections (*lattice*)	25
θ range (lattice)	10.60–18.04°
θ range for data collection	2.64–26.29°
Index ranges	$-12 \leqslant h \leqslant 12, 0 \leqslant k \leqslant 19, 0 \leqslant l \leqslant 16$
Reflections collected	4215
Independent reflections	4038 [$R_{\mathrm{int}} = 0.0337$]
Reflections observed	2566
Criterion for observation	$> 2\sigma$ (I)
Data/parameters	4037/0/317
Final *R* indices [$I > 2\sigma$ (I)]	$R_1 = 0.0297$, $wR_2 = 0.0561$
Goodness-of-fit on F^2	1.000
Final *R* indices (all) R_1/wR_2	0.0829/0.0676
Largest diff. peak and hole	0.614 and -0.580 eÅ^{-3}
Weighting scheme	$w = [1/[S^2(F_o^2)+(0.0237P)^2+0.3454P]$ where $P = (F_o^2+2F_c^2)/3$
Max. and min. transmission	1.000 and 0.486

bulky PPh_3 [P–Pt–P, 97.4°] and short bite angle, S–Pt–N of 68.0° in **3** appear to favour *trans*-PPh_3 and S-bonded $C_5H_4NS^-$ in **2**.

NMR spectral studies

Table 3 contains NMR data (^{1}H, ^{13}C, ^{31}P) for the compounds. The ^{31}P NMR spectrum of **2** (Fig. 2) shows the presence of dissociated PPh_3 in $CDCl_3$ solution according to the equation below.



The NMR spectrum shows that dissociation is not complete, but is considerable. This means that probably **2** and **2a** are in equilibrium, however, there was no evidence for dissociation of both PPh_3 molecules. Since crystals of **2** were grown from CH_3CN, it is possible that this solvent may be acting as a stabiliser of Pt–PPh_3 bonding and as shown by ^{31}P NMR, **2** dissociates in $CHCl_3$ forming **2a** species. The lack of dissociation of **2** in CH_3CN could be attributed to the coordinating properties of CH_3CN presumably along axial sites. Alternatively CH_3CN could interact with the pendant pyridyl group via hydrogen bonding or via delocalised π-electrons on the CN group. This presumably keeps $C_5H_4NS^-$ moiety in S-bonded form with pendant pyridyl group. In contrast, in $CHCl_3$, this stabilisation of the pendant pyridyl group is not available and so it coordinates to Pt(II). It must be emphasised that due to bulky PPh_3 groups with pendant pyridyl groups in *trans* positions, the stereochemical requirements about the Pt(II) center favour dissociation of a PPh_3 group along with chelation by NS-donor set. Low field coordination shift ($\Delta\delta$P, 12.5 ppm) with $^1J_{P-Pt}$ coupling constant of 3866 Hz confirms the coordination of PPh_3 to the Pt metal center.

The absence of ^{1}H NMR signals due to NH in **1**

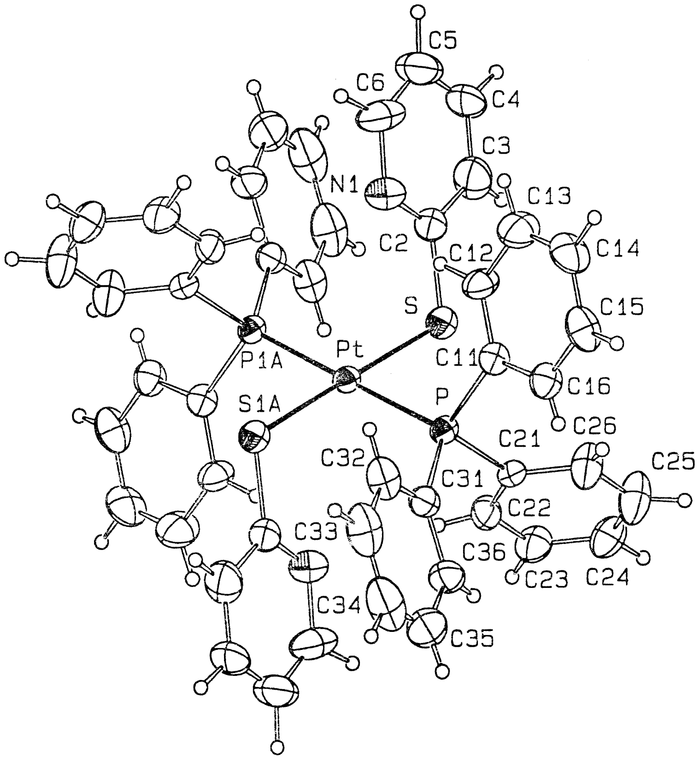


Fig. 1. Perspective view of $[Pt(C_5H_4NS)_2(PPh_3)_2]$ (**2**) molecule with the numbering scheme. The thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms are drawn with an antibitrary radius of 0.1 Å and are represented by open circles.

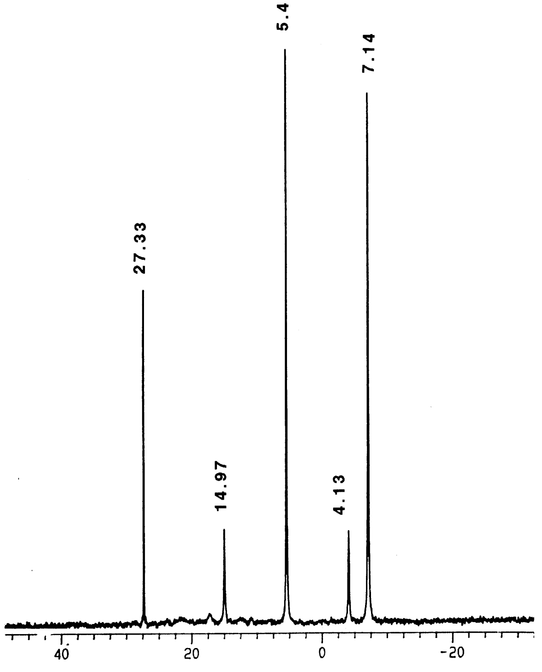


Fig. 2. The ^{31}P NMR spectrum of **2** in $CDCl_3$.

Table 2. Selected bond lengths (Å) and angles (°) for $[Pt(C_5H_4NS)_2(PPh_3)_2]$

Pt–P	2.3147(13)
Pt–S	2.343(2)
S–C(2)	1.739(6)
P–C(31)	1.825(6)
P–C(21)	1.831(5)
P–C(11)	1.841(5)
N(1)–C(2)	1.343(8)
N(1)–C(6)	1.356(8)
C(2)–C(3)	1.416(9)
C(3)–C(4)	1.348(10)
C(4)–C(5)	1.365(13)
C(5)–C(6)	1.376(12)
P–Pt–P*1	180.0
P–Pt–S*1	94.76(5)
P–Pt–S	85.24(5)
S*1–Pt–S	180.0
C(2)–S–Pt	108.2(2)
C(2)–N(1)–C(6)	117.4(7)
N(1)–C(2)–C(3)	120.7(7)
N(1)–C(2)–S	120.7(5)
C(31)–P–C(21)	105.4(3)
C(31)–P–C(11)	100.5(2)
C(21)–P–C(11)	107.1(2)
C(31)–P–Pt	119.7(2)
C(21)–P–Pt	109.8(2)
C(11)–P–Pt	113.4(2)[1]

Symmetry transformations used to generate equivalent atoms: $*1-x,\ -y+1,\ -z$.

Table 3. The ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR data (δ, ppm, J, Hz) of compounds

		H(6)	H(4)	H(3)	H(5)
1		9.10 d	7.36 t	7.20 d	6.91 t
		(J_5, 6.0)	(J_3, 7.6, J_5, 7.6)	(J_4, 8.1)	(J_4, 6.6, J_6, 6.6)
2	set I	8.27 d	7.32 t	7.37 d	6.82 t
		(J_5, 3.4)	(J_3, 7.5, J_5, 7.5)	(J_4, 7.7)	(J_4, 5.9, J_6, 5.9)
	set II	8.09 s[a]	6.65 t[a]	6.68 d[a]	6.52 s[a]
				(J_4, 8.2)	
C_5H_5NS[b]		7.56 ddd	7.34 ddd	7.49 dt	6.73 td
		(J_5, 6.3, J_4, 1.6, J_3, 0.8)	(J_3, 8.7, J_5, 7.0, J_6, 1.8)	(J_4, 8.7, J_5, 0.8, J_6, 0.8)	(J_4, 6.7, J_6, 6.7, J_3, 1.2)
PPh_3 signals		o-H	m- and p-H	free PPh_3	
2		7.39 m	7.56 m	7.14 m	
PPh_3		–	–	7.23 m	

^{13}C NMR		C(2)	C(6)	C(4)	C(5)	C(3)
2	set I[c]	176.5	146.9	136.8	124.9	115.7
	set II[d]	164.9	142.3	135.8	124.9	115.7
C_5H_5NS		175.6	137.0	135.9	132.8	113.1

		PPh$_3$ signals			
		i-C ($^1J_{C-P}$)	o-C ($^2J_{C-P}$)	m-C ($^3J_{C-P}$)	p-C ($^4J_{C-P}$)
PPh_3		132.5 (10.0)	134.2 (19.5)	128.9 (10.8)	129.1 (9.3)
2	set I	128.0 (38.5)	130.7 (6.0)	127.1 (7.5)	130.5 (n.o)
	set II	131.6 (n.o)	132.7 (6.0)	126.9 (6.8)	129.5 (n.o)[e]

^{31}P{^{1}H}	δP	$\Delta\delta$P	$^1J_{P\text{–}Pt}$	
2	5.4[f]	12.5	3866	
PPh_3	−7.14			2

d, doublet; t, triplet, td, triplet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublet; s, singlet.

[a] Broad.

[b] δNH = 13.40 vb.

[c] N,S-chelated $C_5H_4NS^-$.

[d] S-bonded $C_5H_4NS^-$.

[e] n.o., not observed.

[f] Indicates free PPh_3 also.

and **2** confirms that in these compounds anionic $C_5H_4NS^-$ is coordinating to the Pt(II) center. The H(6) proton shows low-field shift relative to free C_5H_5NS in **1** and **2**. The coordination of PPh_3 to Pt(II) leads to a relative up-field shift in **2**. Further, two sets of H(6) proton (and for other protons) shows evidence for both N,S-chelated and S-bonded $C_5H_4NS^-$ moieties in **2a**. Since H(6), in the vicinity of nitrogen, is most sensitive to the coordination changes, the up-field shifts clearly support de-ligation of M–N bond in **2a**. Further, the fact that H(6) proton of N,S-chelated C_5H_4NS (set I) is still up field relative to that of **1**; it reveals increased Pt–N back-bonding when PPh_3 coordinates. De-ligation of Pt–N bond (set II) leads to increased aromaticity, an usual observation in metal–pyridine thiol chemistry [31].

The H(4) proton remains nearly unaffected (**1**; **2a**, set I) when $C_5H_4NS^-$ is N,S-bonded, but moves up-field when it is S-bonded only (**2**,**2a**; set II). H(3) protons also is significantly up-field when $C_5H_4NS^-$ is S-bonded only but is mildly up-field when it is N,S-bonded and finally H(5) protons are also up-field when $C_5H_4NS^-$ is S-bonded only and down-field for N,S-bonded moiety.

^{13}C NMR spectrum of **2** shows unambiguous evidence for N,S-bonded (**2a**, set I, Table 3) and S-bonded (**2**,**2a**, set II) $C_5H_4NS^-$ moieties. All pyridyl carbons except C(5) show low-field shifts (relative to free C_5H_5NS) for N,S-bonded $C_5H_4NS^-$ moiety (**2a**, set I) [31]. The upfield shift in C(2) signal with reduced shifts in positions of C(6) supports the presence of S-bonded $C_5H_4NS^-$ moiety (**2**,**2a**, set II) [31].

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REFERENCES

1. Raper, E. S., *Coord. Chem. Rev.*, 1985, **61,** 115.
2. Raper, E. S., *Coord. Chem. Rev.*, 1996, **153,** 199.
3. Raper, E. S., *Coord. Chem. Rev.*, 1994, **129,** 91.
4. Lobana, T. S. and Bhatia, P. K., *J. Sci. Ind. Res.*, 1989, **48,** 394 (Review).
5. Deeming, A. J., Hardcastle, K. I., Meah, M. N., Bates, P. A., Dawes, H. M. and Hursthouse, M. B., *J. Chem. Soc. Dalton Trans.*, 1988, 227.
6. Karagiannidis, P., Aslanidis, P., Kessissoglou, D. P., Krebs, D. and Dartmann, M., *Inorg. Chim. Acta*, 1989, **156,** 47.
7. Aslanidis, P., Hadjikakou, S. K., Karagiannidis, P., Kojic-Prodic, B. and Luic, M., *Polyhedron*, 1994, **13,** 3119.
8. Mura, P., Olby, B. G. and Robinson, S. D., *J. Chem. Soc. Dalton Trans.*, 1985, 2101.
9. Rosenfield, S. G., Berends, H. P., Gelmini, L., Stephen, D. W. and Mascharak, P. K., *Inorg. Chem.*, 1987, **26,** 2792.
10. Zhang, N., Wilson, S. R. and Shapley, P. A., *Organometallics*, 1988, **7,** 1126.
11. Oro, L. A., Ciriano, M. A., Viguri, F., Tiripicchio-Camellini, A. and Lahoz, F. J., *Nouv. J. Chim.*, 1986, **10,** 75.
12. Deeming, A. J., Meah, M. N., Bates, P. A. and Hursthouse, M. B., *J. Chem. Soc. Dalton Trans.*, 1988, 235.
13. Deeming, A. J., Karim, M., Bates, P. A. and Hursthouse, M. B., *Polyhedron*, 1988, **7,** 1401.
14. Umakoshi, K., Kinoshita, I., Fukui-Yasuba, Y., Matsumoto, K., Ooi, S., Nakai, H. and Shiro, M., *J. Chem. Soc. Dalton Trans.*, 1989, 815.
15. Umakoshi, K., Kinoshita, I., Ichimura, A. and Ooi, S., *Inorg. Chem.*, 1987, **26,** 3557.
16. Wang, S., Staples, R. J., Fackler, J. P. Jr., *Acta Cryst. C*, 1994, **50,** 889.
17. Lobana, T. S. and Paul, S., *Transition Met. Chem.*, 1996, **21,** 300 (and references cited therein).
18. Lobana, T. S., Verma, R., Singh, R. and Castineiras, A., *Transition Met. Chem.*, 1998, **23,** 25.
19. Lobana, T. S., Paul, S. and Castineiras, A., *Polyhedron*, 1997, **16,** 4023.
20. Nakatsu, Y., Nakamura, Y., Matsumoto, K. and Ooi, S., *Inorg. Chim. Acta*, 1992, **196,** 81.
21. Lobana, T. S. and Bhatia, P. K., *Indian J. Chem. Sect. A.*, 1990, **29,** 1225.
22. Delarge, J., *Chem. Abstr.*, 1968, **69,** 2830.
23. ENRAF-NONIUS, CAD 4-Express Software Version 5.1. Enraf-Nonius, Deft, The Netherlands, 1995.
24. Spek, A. L., HELENA, A Program for data collection of CAD4 Data. University of Utrecht, The Netherlands, 1993.
25. Walker, N. and Stuart, D., *Acta Crystallogr. Sect. A*, 1993, **39,** 158.
26. Sheldrick, G. M., *Acta Crystallogr. Sect. A*, 1990, **46,** 467.
27. Sheldrick, G. M., SHELXL 93. Program for the Refinement of Crystal Structures. University of Gottingen, Germany, 1993.
28. International Tables for X-ray Crystallography, Vol. C, Kluwer Academic Publishers. Dordrecht, The Netherlands, 1995.
29. Zsolnai, L., ZORTEP, A Program for the Presentation of Thermal Ellipsoids. University of Heidelberg, Germany, 1994.
30. Wang, S., Fackler, J. P. Jr., *Inorg. Chem.*, 1989, **28,** 2615.
31. Cookson, P. D. and Tiekink, E. R. T., *J. Chem. Soc. Dalton Trans.*, 1993, 259.