Transition-metal Chemistry of Main-group Hydrazides. Part 2.[1] A New Oxime Thiosemicarbazide Framework as a Novel SN Multifunctional Tripodal Ligand for Palladium(II): Synthetic and X-Ray Crystal Structural Investigations†

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Thiosemicarbazide reacted with butane-2,3-dione oxime to give a Schiff-base product HL *via* the selective reaction of the hydrazine nitrogen atom. The ligating properties of this new oxime thiosemicarbazide ligand L with palladium(II) were investigated and in the complex [PdL(Cl)] **1** the palladium(II) atom is bound in a trimodal, *cis* arrangement to the oxime nitrogen, hydrazine nitrogen and the sulfur centre. The crystal structure of complex **1** further reveals that the oxime thiosemicarbazide HL has reacted with $[PdCl_2(PhCN)_2]$ presumably *via* the elimination of HCl, in the thiol rather than the thione form. The hydrogen-bonding interaction of the oxime hydrogen that caused HL to be a dimer in the solid state is lost upon complexation with palladium(II), giving complex **1** a monomeric structure. X-Ray crystal data; for HL, monoclinic, space group $P2_1/c$, $a = 11.082(4)$, $b = 12.679(2)$, $c = 6.101(2)$ Å, $Z = 4$, $R = 0.044$ and $R' = 0.064$; **1**, triclinic, space group $P\bar{1}$, $a = 7.660(3)$, $b = 12.972(5)$, $c = 22.325(8)$ Å, $\alpha = 89.26(3)$, $\beta = 81.53(3)$, $\gamma = 84.75(3)°$, $Z = 8$, $R = 0.045$ and $R' = 0.064$.

Thiosemicarbazide $[NH_2C(S)NHNH_2]$ belongs to the family of hydrazine-based ligands with multifunctional donor centres.[1-9] The application of thiosemicarbazide-based ligands for bonding to transition metals is of fundamental importance in understanding the organometallic and co-ordination chemistries of derivatized hydrazines and also enhances the scope and subsequent utility of the nitrogen family of ligands in transition-metal chemistry.[1,10-15] In addition, the proven pharmacological importance of thiosemicarbazide-based ligands and their metal complexes has prompted renewed interest in the main-group and transition-metal chemistry of such compounds.[16-21] As part of our on-going studies on the functionalization of main-group hydrazides, we are currently investigating the reactions of aldehydes and ketones with carbohydrazides. In this context we have studied the Schiff-base reaction of thiosemicarbazide with butane-2,3-dione oxime. In this paper we report (*a*) the regioselectivity observed in the Schiff-base coupling reaction of butane-2,3-dione oxime with thiosemicarbazide to produce an oxime-functionalized thiosemicarbazide, (*b*) the dehydrochlorination of $[PdCl_2(PhCN)_2]$ in its reaction with the new ligand to produce a new palladium(II) complex and (*c*) the X-ray crystal structural features of the new ligand and the metal complex.

Experimental

Physical Measurements and Instrumentation.—Nuclear magnetic resonance spectra were recorded on a Bruker WH-500 spectrometer and the chemical shifts are reported in ppm downfield from external standard $SiMe_4$. Infrared spectra were obtained using Nujol mulls and KBr cells on a Mattson Galaxy 3000 spectrophotometer. Elemental analyses of the new compounds were performed by Oneida Research Services, Inc., New York.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

High-performance liquid chromatographic (HPLC) analysis of the new compounds was performed on a Hamilton PRP-1 reversed-phase column with a Beckman Series 332 dual-pump gradient system. A Waters model 440 UV absorbance detector connected to a strip-chart recorder was used to check the UV absorbance. Water and acetonitrile were used as the mobile phase at a flow rate of 1.0 $cm^3\ min^{-1}$. Initial elution was for 2 min at 1 $cm^3\ min^{-1}$ with 100% water. During the next 3 min a gradient was applied from 0 to 100% MeCN. This concentration was maintained for 10 min after which another gradient was applied to return the column to its original condition.

Reagents and Materials.—Reagents such as butane-2,3-dione oxime, thiosemicarbazide and $PdCl_2$ were purchased from Aldrich and were used without further purification. The compound $[PdCl_2(PhCN)_2]$ was prepared according to the literature method.[22] All reactions were carried out under anaerobic and anhydrous conditions using prepurified N_2 and conventional Schlenk techniques.

Synthesis of the Oxime Thiosemicarbazide Ligand HL.—To a solution of thiosemicarbazide (2 g, 22 mmol) in tetrahydrofuran (thf) (100 cm^3) was added dropwise with stirring a solution of butane-2,3-dione oxime (2.22 g, 22 mmol) in thf (100 cm^3). The mixture was heated under reflux for 6 h before the solvent was removed *in vacuo* to obtain a crystalline solid HL. Recrystallization from boiling acetonitrile gave crystalline samples of HL (3.45 g, 90%; m.p. 197 °C) (Found: C, 34.45; H, 5.75; N, 32.15. Calc. for $C_5H_{10}N_4OS$: C, 34.50; H, 5.80; N, 32.20%). NMR $[(CD_3)_2CO]$: ^1H, δ 2.1 (s, 3 H, N=CMe) and 2.25 (s, 3 H, CCMe); ^{13}C, δ 11.04 (s, N=C*Me*), 147.50 (s, C=N), 155.074 (s, C=NOH) and 181.11 (s, C=S).

Synthesis of [PdL(Cl)] **1**.—A solution of $[PdCl_2(PhCN)_2]$ (1.77 g, 4.61 mmol) in thf (100 cm^3) was added dropwise (15 min) at room temperature to a solution of HL (803 mg, 4.61 mmol) also in thf (100 cm^3). The mixture was stirred for 6 h before the solvent was removed *in vacuo* to obtain complex **1** as

Table 1 Crystallographic data for the oxime thiosemicarbazide HL and complex **1**

	HL	**1**
Formula	$C_5H_{10}N_4OS$	$C_5H_9ClN_4OPdS$·0.5MeCN
M	174.22	335.62
Crystal size/mm	0.10 × 0.40 × 0.53	0.05 × 0.07 × 0.40
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	11.082(4)	7.660(3)
b/Å	12.679(2)	12.972(5)
c/Å	6.101(2)	22.325(8)
α/°		89.26(3)
β/°	104.520(20)	81.53(3)
γ/°		84.75(3)
U/Å^3	829.9(4)	2184.9(14)
Z	4	8
D_c/gm^{-3}	1.394	2.040
$F(000)$	368	1320
$2\theta_{max}$/°	50	40
μ/cm^{-1}	33.0	58.0
h,k,l Range	0–13, −15 to 0, −7 to 7	−7 to 7, 0–12, −21 to 21
Total data	1530	4519
Unique data	1456	4074
Observed data [$I \geqslant 2.5\sigma(I)$]	1127	2852
R^a	0.044	0.045
R'^b	0.064	0.064

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$, $w^{-1} = [\sigma^2|F_o| + 0.0008(F_o)^2]$.

Table 2 Atomic positional coordinates with estimated standard deviations (e.s.d.s) in parentheses for HL

Atom	x	y	z
S	0.5574(7)	0.6565(6)	0.1735(11)
N(1)	0.5974(3)	0.4604(22)	0.3254(4)
C(2)	0.6158(24)	0.5617(22)	0.3632(4)
N(3)	0.6885(23)	0.5895(2)	0.5689(4)
N(4)	0.7330(21)	0.5119(18)	0.7249(4)
C(5)	0.8050(24)	0.5391(21)	0.9157(4)
C(6)	0.8462(3)	0.4507(22)	1.0721(4)
N(7)	0.9188(23)	0.4748(18)	1.2651(4)
O	0.9540(24)	0.3862(17)	1.4041(4)
C(8)	0.8472(3)	0.6490(22)	0.9809(5)
C(9)	0.8029(3)	0.3411(23)	1.0043(6)

an orange microcrystalline solid. Slow evaporation of acetonitrile solutions of complex **1** gave analytically pure crystals of X-ray diffraction quality [1.1 g, 87%; m.p. 243 °C (decomp.)] (Found: C, 21.15; H, 3.15; N, 19.75. Calc. for $C_5H_9ClN_4OPdS$: C, 21.2; H, 3.20; N, 19.80%). NMR (Me_2SO): ^{1}H, δ 2.09 (s, 3 H, N=CMe), 2.13 (s, 3 H, CCMe) and 11.42 (NOH); ^{13}C, 13.16 (s, CC*Me*), 13.97 (s, N=C*Me*), 152.31 (s, C=N), 152.31 (s, C=NOH) and 179.72 (s, C=S).

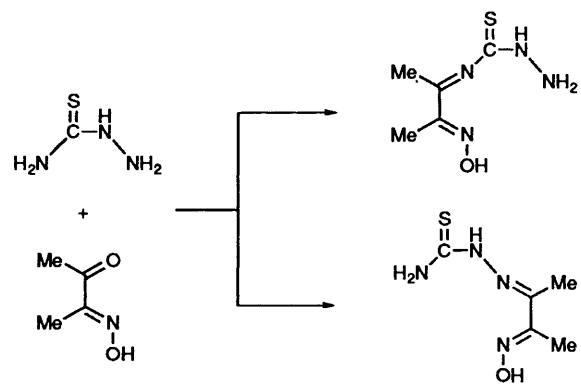
X-Ray Data Collection and Processing.—White, needle-shaped crystals of HL and orange, block-like crystals of complex **1** were isolated from slow evaporations of thf and MeCN solutions respectively. All X-ray data were collected on an Enraf-Nonius CAD4 diffractometer, operating in the θ–2θ scan mode, with Mo-Kα radiation and a graphite monochromator at 22 ± 1 °C. Crystal data and details of the data collection are given in Table 1. The positional parameters and selected bond distances and angles of HL and complex **1** are in Tables 2–5. All the hydrogen-atom parameters were calculated from the idealized geometry.

The structure was solved by the Patterson method and refined by least squares, which minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma^2(\text{counting}) + 0.008(F_o)^2/4F_o]$. Atomic scattering factors which included anomalous scattering contributions were from ref. 23 and the program used for the crystallographic computations from ref. 24. All the hydrogen atoms were introduced in the last step of the refinement procedure in calculated positions. The final agreement factor (R) for HL was 0.044 and the highest peak in the final Fourier-difference map was 0.35 e Å^{-3}. The number of observed data for complex **1** was limited due to the small crystal volume and poor crystal quality and for this reason, only the Pd, S and Cl atoms were refined with anisotropic thermal parameters. The final cycle of the least-square refinement gave R 0.045 and the highest peak in the last Fourier-difference synthesis, located close to the metal atom, was 0.89 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 3 Selected bond distances (Å) and angles (°) for HL

S–C(2)	1.681(3)	C(5)–C(6)	1.469(4)
N(1)–C(2)	1.312(4)	C(5)–C(8)	1.492(4)
C(2)–N(3)	1.357(3)	C(6)–N(7)	1.285(3)
N(3)–N(4)	1.372(3)	C(6)–C(9)	1.495(4)
N(4)–C(5)	1.283(3)	N(7)–O	1.403(3)
S–C(2)–N(1)	124.3(20)	N(4)–C(5)–C(8)	125.2(24)
S–C(2)–N(3)	119.2(21)	C(6)–C(5)–C(8)	120.9(22)
N(1)–C(2)–N(3)	116.5(24)	C(5)–C(6)–N(7)	115.8(24)
C(2)–N(3)–N(4)	118.8(23)	C(5)–C(6)–C(9)	120.2(23)
N(3)–N(4)–C(5)	118.0(23)	N(7)–C(6)–C(9)	123.9(3)
N(4)–C(5)–C(6)	113.9(23)	C(6)–N(7)–O	112.3(22)



Scheme 1

Results and Discussion

The reaction of butane-2,3-dione oxime with thiosemicarbazide in thf produced a white, crystalline, air-stable solid. Two products are possible (Scheme 1) as the Schiff-base coupling reaction could occur at two different NH_2 centres. However, the HPLC analysis of the reaction product showed a single peak (R_t = 6.5 min) indicating the regioselectivity of the reaction. The Schiff-base coupling, in fact, has selectively occurred at the hydrazine nitrogen as confirmed by an X-ray crystallographic analysis of this new oxime thiosemicarbazide HL. The ORTEP[25] plot of this ligand in Fig. 1 shows its dimeric composition in the solid state as a result of the hydrogen-bonding interaction of the oxime group. The fractional atomic coordinates and selected bonding parameters are summarized in Tables 2 and 3 respectively. Similar to the configuration observed in the parent thiosemicarbazide, the sulfur and the hydrazine nitrogen atoms of HL are *trans* to one another. The structure is further characterized by the effective planarity of all the non-hydrogen atoms, a feature that is common to the parent

Table 4 Atomic positional coordinates with e.s.d.s in parentheses for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	0.1084(16)	0.2109(9)	0.0480(5)	C(2C)	0.2588(20)	0.9884(12)	0.3130(7)
S(A)	0.0778(5)	0.0409(3)	0.0601(18)	N(3C)	0.3055(16)	0.9091(10)	0.2754(6)
N(1A)	0.1692(17)	−0.0613(10)	0.1562(6)	N(4C)	0.3834(16)	0.8251(9)	0.3036(5)
C(2A)	0.1460(19)	0.0339(11)	0.1326(7)	C(5C)	0.4371(20)	0.7406(12)	0.2726(7)
N(3A)	0.1831(15)	0.1142(9)	0.1623(5)	C(6C)	0.5136(21)	0.6565(12)	0.3110(7)
N(4A)	0.1709(16)	0.2043(9)	0.1303(5)	N(7C)	0.5125(16)	0.6840(9)	0.3636(5)
C(5A)	0.2049(19)	0.2898(11)	0.1526(6)	O(C)	0.5809(15)	0.6104(9)	0.4045(5)
C(6A)	0.1919(19)	0.3825(12)	0.1149(7)	C(8C)	0.4258(21)	0.7273(12)	0.2087(7)
N(7A)	0.1565(16)	0.3586(9)	0.0616(5)	C(9C)	0.5784(21)	0.5530(12)	0.2849(7)
O(A)	0.1444(14)	0.4410(8)	0.0195(5)	Cl(C)	0.4505(6)	0.8091(3)	0.4888(19)
C(8A)	0.2551(19)	0.2990(11)	0.2142(7)	Pd(4)	0.9718(16)	0.7045(9)	0.3104(5)
C(9A)	0.2083(21)	0.4899(12)	0.1337(7)	S(D)	0.9124(6)	0.7263(3)	0.2155(19)
Cl(A)	0.0469(6)	0.2334(3)	−0.0499(18)	N(1D)	0.7589(17)	0.9010(10)	0.1788(6)
Pd(2)	0.6975(16)	0.3454(9)	0.1257(5)	C(2D)	0.8144(19)	0.8543(11)	0.2285(7)
S(B)	0.7607(5)	0.3205(3)	0.2207(18)	N(3D)	0.7992(16)	0.9049(10)	0.2782(6)
N(1B)	0.7633(17)	0.1360(10)	0.2701(6)	N(4D)	0.8624(15)	0.8450(9)	0.3240(5)
C(2B)	0.7329(21)	0.1869(12)	0.2222(7)	C(5D)	0.8510(20)	0.8834(12)	0.3781(7)
N(3B)	0.6862(16)	0.1341(9)	0.1761(5)	C(6D)	0.9324(20)	0.8093(12)	0.4217(7)
N(4B)	0.6621(16)	0.1979(9)	0.1280(5)	N(7D)	0.9923(17)	0.7233(10)	0.3977(6)
C(5B)	0.6169(20)	0.1597(11)	0.0783(7)	O(D)	1.0730(14)	0.6522(8)	0.4355(5)
C(6B)	0.6017(20)	0.2335(12)	0.0303(7)	C(8D)	0.7677(21)	0.9884(12)	0.3974(7)
N(7B)	0.6309(15)	0.3276(9)	0.0431(5)	C(9D)	0.9317(22)	0.8390(13)	0.4850(8)
O(B)	0.6130(14)	0.4020(8)	−0.0021(5)	Cl(D)	1.1016(6)	0.5372(3)	0.3046(19)
C(8B)	0.5811(20)	0.0499(12)	0.0719(7)	N(S1)	0.9545(19)	0.2507(12)	0.3624(7)
C(9B)	0.5578(21)	0.2043(12)	−0.0315(7)	C(1S1)	0.8983(22)	0.3189(13)	0.3921(7)
Cl(B)	0.7300(6)	0.5194(3)	0.1181(18)	C(2S1)	0.8218(23)	0.4066(13)	0.4326(8)
Pd(3)	0.4059(16)	0.8260(9)	0.3895(5)	N(S2)	0.2810(3)	0.4316(16)	0.4494(9)
S(C)	0.2756(6)	0.9882(3)	0.3908(19)	C(1S2)	0.3360(25)	0.3709(15)	0.4141(8)
N(1C)	0.1855(18)	1.0765(10)	0.2920(6)	C(2S2)	0.4120(25)	0.2909(14)	0.3700(8)

Table 5 Selected bond distances (Å) and angles (°) for complex **1**

Pd–S	2.247(4)	N(1)–C(2)	1.343(19)
Pd–N(4)	1.965(12)	C(2)–N(3)	1.317(19)
Pd–N(7)	2.019(12)	C(4)–C(5)	1.286(19)
Pd–Cl	2.311(4)	C(5)–C(6)	1.462(20)
S–C(2)	1.773(15)	C(6)–N(7)	1.306(19)
		N(7)–O	1.420(16)
S–Pd–N(4)	85.0(4)	S–C(2)–N(1)	116.3(11)
S–Pd–N(7)	163.1(4)	S–C(2)–N(3)	124.3(11)
S–Pd–Cl	100.1(16)	N(1)–C(2)–N(3)	119.3(13)
N(4)–Pd–N(7)	78.1(5)	C(2)–N(3)–N(4)	112.9(11)
N(4)–Pd–Cl	174.5(4)	Pd–N(4)–N(3)	122.8(9)
N(7)–Pd–Cl	96.7(4)	Pd–N(4)–C(5)	116.4(10)
Pd–S–C(2)	94.8(5)		

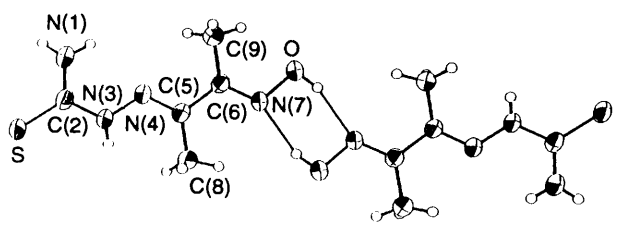


Fig. 1 An ORTEP representation of the structure of HL. The thermal ellipsoids are drawn at the 50% probability level

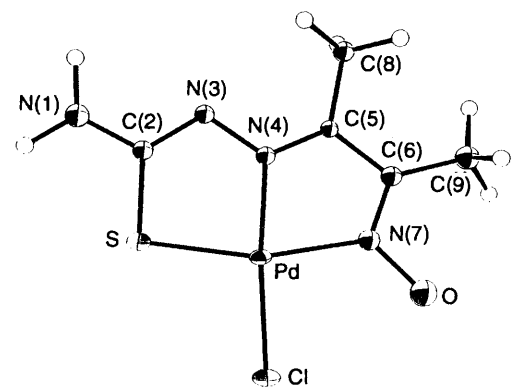
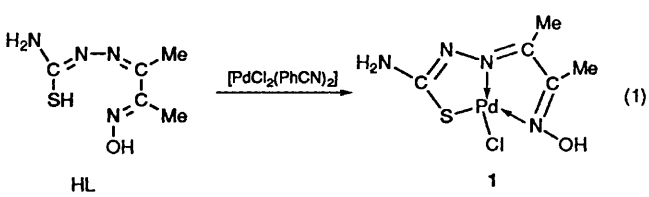
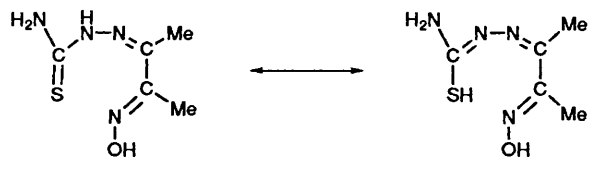


Fig. 2 An ORTEP representation of the structure of complex **1**. The thermal ellipsoids are drawn at 50% probability level



structure. The addition of an oxime unit to the backbone of thiosemicarbazide, as in HL, causes no significant change in the C–S, C(2)–N(1), C(2)–N(3) and N(3)–N(4) bond distances.

We have investigated the ligating properties of L by interacting it with $[PdCl_2(PhCN)_2]$ in thf [equation (1)]. Single crystals of the new palladium(II) complex **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of acetonitrile solutions. The ORTEP[25] plot of complex **1** (Fig. 2) shows the remarkable co-ordination features of the oxime thiosemicarbazide ligand with the palladium(II) centre. The poor quality of the crystals resulted in the refinement of only the Pd, S and Cl atoms with anisotropic thermal parameters. However, solution molecular-weight measurements and the C, H, N and Cl analysis of complex **1** unequivocally confirmed the chemical compositions shown in Fig. 2. The fractional atomic coordinates and selected crystallographic parameters are summarized in Tables 4 and 5 respectively. The monomeric structure of complex **1** is comprised of a *cis* arrangement of the sulfur, hydrazine nitrogen and oxime nitrogen atoms around the palladium(II) centre. The hydrogen-bonding interaction of the oxime hydrogen that caused HL to be a dimer in the solid state (Fig. 1) is lost upon complexation with palladium (Fig. 2).



I II

The Pd atom is in a square-planar environment defined by the chlorine and sulfur, oxime [N(7)] and hydrazino [N(4)] nitrogen atoms. There is a slight elongation of the oxime C=N bond on going from HL [C(6)–N(7) 1.285(3) Å] to the palladium(II) complex [C(6)–N(7) 1.306(19) Å] presumably a consequence of the bond formation between the oxime nitrogen and the palladium(II) centre. The thiocarbonyl bond distance in complex **1** [C(2)–S 1.773(15) Å] is longer than it is in the uncomplexed ligand [C(2)–S 1.681(3) Å] and the Pd–S distance, 2.247(4) Å, is within the range observed for compounds containing Pd–S σ bonds.[26] It appears that there is a slight tetrahedral distortion at the palladium atom, as evidenced by the S–Pd–N(7) and Cl–Pd–N(4) angles of 163.1(4) and 174.5(4)°, respectively.

The bidentate chelating interactions through the sulfur and hydrazinic nitrogens is well known in the transition-metal chemistry of thiosemicarbazides. However, the co-ordination of the ligand L to the palladium(II) centre in complex **1** as shown in the present investigation occurs in a trimodal fashion and reflects the diversity in the reactions of functionalized thiosemicarbazides. The dehydrochlorination of $[PdCl_2(PhCN)_2]$ to produce complex **1** can be rationalized through the reaction of the metal halide with the tautomeric form **II** rather than **I**. Therefore, ligands such as HL can function as uninegative anions in their reactions with metal halides. In fact, the parent thiosemicarbazide has also been shown to exist in the thione (**I**) and thiol (**II**) tautomeric forms, the reactions of both forms with transition metals having received some attention.

Conclusion

The selectivity and the near quantitative yield of the product of the Schiff-base coupling reaction of thiosemicarbazide with butane-2,3-dione oxime is of note. The present investigation also demonstrates that the chemical modification of the thiosemicarbazide backbone is a fruitful way of generating multifunctional hydrazine-based ligand systems. The trimodal co-ordination of palladium(II) as in complex **1** illustrates the potential of the versatile reactivity of the oxime thiosemicarbazide ligand with transition-metal precursors.

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References

1 Part 1, K. V. Katti, P. R. Singh and C. L. Barnes, *Inorg. Chem.*, 1992, **31**, 4588.
2 M. A. Ali and S. E. Livingstone, *Coord. Chem. Rev.*, 1975, **15**, 279.
3 C. F. R. S. Vagg, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, pp. 793–812.
4 M. A. Ali and S. E. Livingstone, *Coord. Chem. Rev.*, 1974, **13**, 101.
5 M. Bellichi Ferrari, G. Gaspari Fava, C. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1992, 2153.
6 M. Belicchi Ferrari, G. Gaspari Fava, C. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1991, 1951.
7 E. N. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 1991, 2125.
8 D. Chattopadhyay, S. K. Mujundar, P. Lowe, C. H. Schwalbe, S. K. Chattopadhyay and S. Ghosh, *J. Chem. Soc., Dalton Trans.*, 1991, 2121.
9 N. Belicchi Ferrari, G. Gaspari Fava, M. Lanfranchi, C. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta*, 1991, **181**, 253.
10 M. Belicchi Ferrari, G. Gaspari Fava, C. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1989, 361.
11 M. J. Abrams, S. K. Larsen and J. Zubieta, *Inorg. Chem.*, 1991, **30**, 2031.
12 T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 2094.
13 C. M. Archer, J. R. Dilworth, P. Jobanputra, R. M. Thompson, M. McPartin, D. C. Povey, G. W. Smith and J. D. Kelly, *Polyhedron*, 1990, **9**, 1497.
14 P. J. Shepiro, L. M. Henling, R. E. Marsh and J. E. Bercaw, *Inorg. Chem.*, 1990, **29**, 4560.
15 R. C. Murray and R. R. Schrock, *J. Am. Chem. Soc.*, 1985, **107**, 4557.
16 B. F. G. Johnson, B. L. Haymore and J. R. Dilworth, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. G. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, pp. 99–159 and refs. therein.
17 D. H. Petering and H. G. Petering, *Handbook of Experimental Pharmacology*, eds. C. Sartorelli and D. G. Johns, Springer, Berlin, 1975, p. 841.
18 D. H. Petering, W. E. Antholine and L. A. Saryan, *Anticancer and Interferon Agents, Synthesis and Properties*, eds. L. A. Saryan and G. B. Butler, Marcel Dekker, New York, 1984, p. 203.
19 F. A. French and E. J. Blanz, jun., *Cancer Res.*, 1965, **25**, 45.
20 D. H. Petering, *Adv. Exp. Med. Biol.*, 1978, **91**, 179.
21 D. H. Petering, in *Metal Ions in Biological Systems*, ed. H. Sigel, Marcel Dekker, New York, 1980, vol. 11, p. 197.
22 M. S. Kharasch, R. C. Seylor and F. R. Mayo, *J. Am. Chem. Soc.*, 1938, **60**, 882.
23 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
24 E. J. Gabe, Y. LePage, J.-P. Charland and F. E. Lee, *J. Appl. Crystallogr.*, 1989, **22**, 384.
25 C. K. Johnson, ORTEP II, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
26 G. R. Giesbrecht, G. S. Hanan, G. E. Kickham and S. J. Loeb, *Inorg. Chem.*, 1992, **31**, 3291.

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