

Mononuclear cobalt carbonyls containing monodentate thiolate or xanthate groups. The structures of $\text{PhSCo}(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ and $\text{MeOCS}_2\text{Co}(\text{CO})_2(\text{PPh}_2^i\text{Bu})_2$

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Abstract

Complexes of the type $\text{PhSCo}(\text{CO})_2\text{L}_2$ (**1**; L = phosphine or phosphite) and the complex $\text{MeOCS}_2\text{Co}(\text{CO})_2(\text{PPh}_2^i\text{Bu})_2$ (**5**) have been prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, CO, the appropriate phosphine or phosphite, and $\text{PhSH} + \text{NaOMe}$ or MeOCS_2K , respectively. The crystal structures of **1a** (L = PPh_2OMe) and **5** · MeCN have been determined. These compounds are the first structurally characterized cobalt carbonyl complexes containing a monodentate thiolate or xanthate group.

Introduction

Mononuclear cobalt carbonyl derivatives with monodentate thiol or thiolate groups, such as $\text{HSCo}(\text{CO})_4$ or $\text{RSCo}(\text{CO})_4$, have been repeatedly proposed as intermediates in reactions of sulfur-containing compounds catalyzed by cobalt carbonyls [1–3], and analogous compounds probably also play a role in some similar reactions [4–8]. Most cobalt carbonyl derivatives containing thiolate groups which have been described and well characterized previously are, however, cluster complexes composed of 3–6 cobalt atoms in which the RS groups act as bridging μ_2 - or μ_3 -ligands [9–16]. Only quite recently has IR spectroscopic evidence been presented for the existence of $\text{RSCo}(\text{CO})_4$ type complexes (stable below -40°C) and $\text{PhCH}_2\text{SCo}(\text{CO})_3(\text{PPh}_3)$ (isolated as a light brown precipitate) [17].

We now report the preparation and the first structural characterization of cobalt carbonyl derivatives containing monodentate thiolate groups with the general formula $\text{RSCo}(\text{CO})_2\text{L}_2$ (**1**; L = phosphine or phosphite), and the crystal structure of

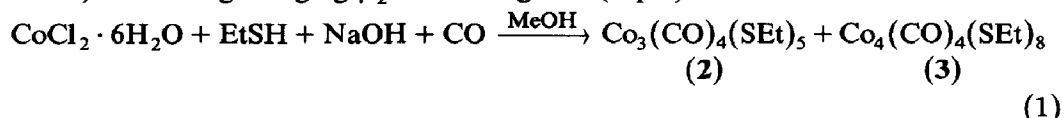
one representative, $\text{PhSCo}(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ (**1a**). These complexes may be regarded as models of the $\text{RSCo}(\text{CO})_4$ -type intermediates proposed for the above-mentioned reactions.

On the basis of these results, and also including xanthates as sulfur-containing reactants in our investigations we also prepared and characterized by X-ray spectroscopy the analogous complex $\text{MeOCS}_2\text{Co}(\text{CO})_2(\text{PPh}_2^i\text{Bu})_2$ (**5**), a cobalt carbonyl derivative containing a monodentate xanthate group.

Results and discussion

Synthesis of the complexes

As previously reported [10], cobalt(II) salts in methanol solution absorb CO in the presence of ethanethiol and a base to yield polynuclear carbonyl complexes (**2** and **3**) containing bridging μ_2 -thiolate ligands (Eq. 1):



When this reaction was performed in the presence of PPh_3 , a mixture of two, closely related cobalt carbonyl complexes (**4a** and **4b**) was formed and these could be only partly separated by chromatography. The two compounds have rather similar IR spectra in hexane solution (**4a**: 2010s, 1999s, and 1787m; **4b**: 2002s, 1998vs, 1807m, cm^{-1}), and are thought to be the two possible isomers of the PPh_3 -substituted derivative of **2**, as shown in Fig. 1. This assignment is based on the observation that one of these complexes, **4a** is also formed in a slow reaction when PPh_3 is added to a hexane solution of **2** and on the closely related IR spectra of the two complexes. The available information is not sufficient, however, to decide which of the two structures shown on Fig. 1 belongs to **4a** or **4b**.

The reaction took a completely different course when thiophenol was used instead of ethanethiol in the presence of different phosphines or phosphites such as PPh_2^iBu , $\text{PPh}_2(\text{OMe})$, PEt_2OPh , $\text{P}(\text{OMe})_3$, or PPh_2H . In these cases, no cobalt carbonyl clusters were formed, but instead mononuclear complexes of the type $\text{PhSCo}(\text{CO})_2\text{L}_2$ (**1**; L = phosphine or phosphite), as shown by the IR spectra of the methanolic reaction products (giving two bands around 1920s and 1980s cm^{-1} , characteristic of complexes of the type $\text{XCo}(\text{CO})_2\text{L}_2$ [18,19]), and the isolation and characterization of two representatives of this class of compounds, $\text{PhSCo}(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ (**1a**) and $\text{PhSCo}(\text{CO})_2(\text{PPh}_2^i\text{Bu})_2$ (**1b**):

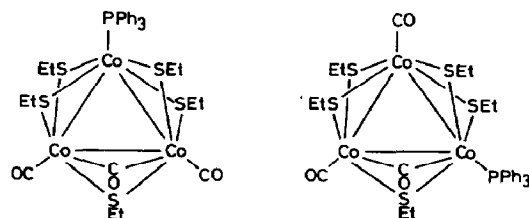
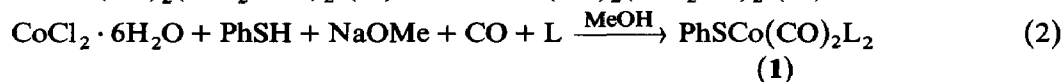


Fig. 1. Proposed structures for complexes **4a** and **4b**.

Table 1

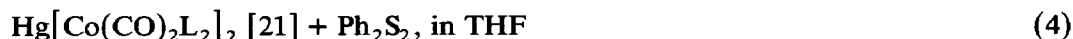
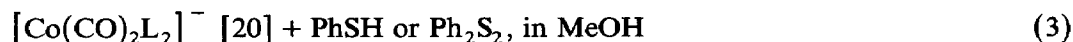
IR spectra of the complexes $\text{PhSCo(CO)}_2\text{L}_2$ (**1**) and $\text{MeOCS}_2\text{Co(CO)}_2(\text{PPh}_2^i\text{Bu})_2$ (**5**) in the C–O stretching region in THF solution

Complex	Ligand	$\nu(\text{CO})$, cm^{-1}
1a	PPh_2OMe	1925vs, 1981s
1b	PPh_2^iBu	1912vs, 1970s
1c	PEt_2OPh	1920vs, 1980s
1d	P(OMe)_3	1940vs, 2000s
1e	PPh_2H	1926vs, 1984s
5		1920vs, 1979s

Later we found that for preparative purposes THF is a better solvent for the reaction than methanol (although in this case the reaction mixture is initially a slurry) because the complexes **1a** and **1b** could be obtained pure much more easily (see Experimental section). The IR spectra data for THF solutions of the complexes **1a**–**1e** prepared in this way are listed in Table 1. Complexes **1c**–**1e** were obtained only in solution and not isolated in pure form.

We were able to show that Co^{II} is reduced to Co^{I} , at least in part, by the phosphine, since $i\text{BuPh}_2\text{PO}$ was observed as a by-product in the synthesis of $\text{PhSCo(CO)}_2(\text{PPh}_2^i\text{Bu})_2$.

The tendency towards formation of complexes of type **1** is rather strong; from their characteristic infrared spectra they were also identified as the main products from the following reaction mixtures under an atmosphere of CO:



Most of these systems were examined with several of the above mentioned ligands; the reaction starting from $\text{Hg}[\text{Co(CO)}_2\text{L}_2]_2$ (reaction 4) with $\text{L} = \text{PPh}_2\text{OMe}$ was developed into an alternative preparative method for the synthesis of **1a** (see Experimental section).

As already reported [23], a methanolic solution of CoCl_2 and MeOCS_2K reacts with CO to yield the cluster $\text{Co}_3(\text{CO})_7(\text{S})(\text{S}_2\text{COMe})$, which can be transformed by PPh_3 in a separate reaction into its monosubstituted derivative $\text{Co}_3(\text{CO})_6(\text{PPh}_3)(\text{S})(\text{S}_2\text{COMe})$. We have now found that if the reaction with CO is performed in the presence of PPh_2^iBu there is a completely different outcome, and the mononuclear complex $\text{MeOCS}_2\text{Co(CO)}_2(\text{PPh}_2^i\text{Bu})_2$ (**5**) is formed. Complex **5** crystallized from MeCN as $\text{MeOCS}_2\text{Co(CO)}_2(\text{PPh}_2^i\text{Bu})_2 \cdot \text{MeCN}$, and was isolated in this form in good yield; a crystal structure determination shows that it contains the xanthate group as a monodentate ligand. Its IR spectrum in THF solution is very similar to that of complexes **1** (see Table 1).

The ease of formation of type **1** complexes, as well as of that of complex **5** from Co^{2+} , PR_3 , and CO in the presence of an appropriate sulfur-containing ligand and a base, suggests that this reaction may provide a rather general route to cobalt

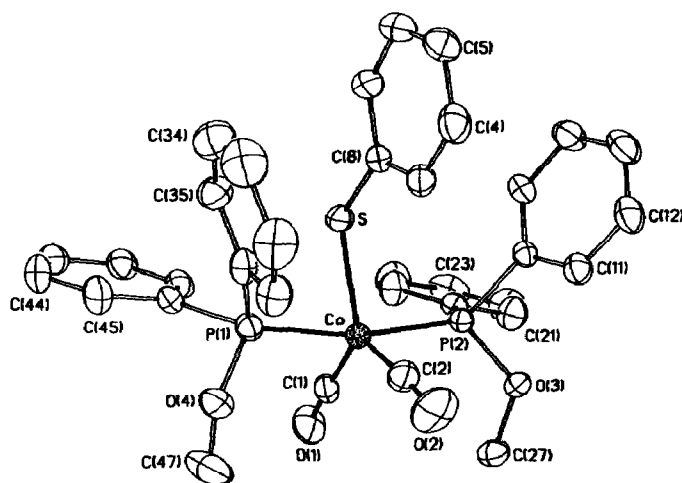


Fig. 2. The molecular structure of **1a** drawn with 40% thermal ellipsoids.

carbonyl complexes having the composition $\text{XCo(CO)}_2\text{L}_2$, and we are currently exploring this possibility.

Structures of the complexes

The structures of complexes **1a** and **5** are shown in Fig. 2 and 3, respectively, and Table 2 lists selected bond distances and angles for the two compounds. Both compounds have distorted trigonal bipyramidal structures, with the phosphine ligands occupying the two apical positions and the sulfur-containing ligand one of the equatorial positions.

No structural information has been available until now on cobalt carbonyl derivatives containing a thiolate group as a terminal ligand. The Co–S distance of 2.299(1) Å in complex **1a** can therefore be compared only with the values for the complexes $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SPh})_4]$ (2.316–2.342 Å) [24], $(\text{Me}_4\text{N})_2[\text{Co}_4(\text{SPh})_{10}]$ (2.254–2.263 Å) [25], and $[\text{Co}(\text{S}-2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2)_2(\text{py})_2]$ (2.253–2.272 Å) [26] which contain

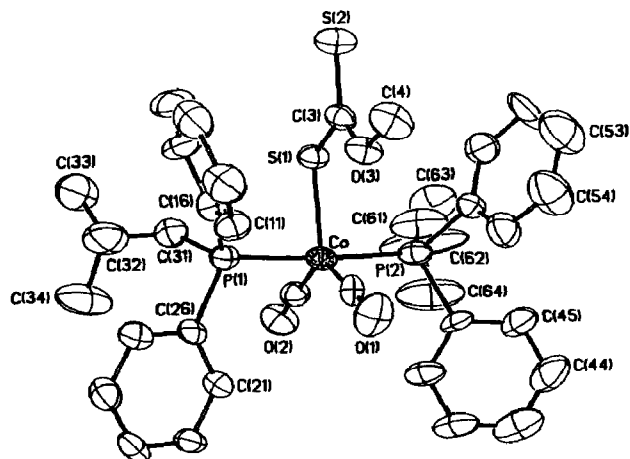


Fig. 3. The molecular structure of **4** drawn with 40% thermal ellipsoids.

Table 2

Selected bond distances (Å) and angles (°) in **1a** and **5**

	1a	5
<i>Bond distances</i>		
Co–P(1)	2.181(1)	2.206(3)
Co–P(2)	2.183(1)	2.209(3)
Co–S	2.299(1)	2.315(3)
Co–C(1)	1.749(5)	1.744(10)
Co–C(2)	1.757(5)	1.726(12)
<i>Bond angles</i>		
P(1)–Co–P(2)	167.7(1)	175.5(1)
P(1)–Co–S	82.4(1)	87.1(1)
P(2)–Co–S	85.9(1)	88.8(1)
P(1)–Co–C(1)	95.7(1)	89.5(3)
P(1)–Co–C(2)	91.8(1)	90.9(3)
P(2)–Co–C(1)	92.6(1)	89.9(3)
P(2)–Co–C(2)	92.1(1)	93.0(3)
C(1)–Co–C(2)	119.0(2)	128.1(5)
Co–S–C(8)	114.0(1)	
Co–S–C(3)		110.2(4)

terminal SAr ligands, and with the values (2.200–2.369 Å) for those cobalt carbonyl clusters which contain doubly or triply bridging SEt groups [12–15]. The rather wide range of these bond distances suggests that the Co–S bond easily adjusts itself to the overall electronic and steric requirements of the whole molecule, and its strength is more a function of these factors than of the terminal or bridging character of the thiolate ligand.

The Co–S bond length in complex **5** (2.315(3) Å), on the other hand, clearly reflects the monodentate character of the xanthate ligand. In the two other structurally characterized cobalt complexes containing xanthate groups, $\text{Co}(\text{S}_2\text{COEt})_3$ [27] and $\text{Co}_3(\text{CO})_6(\text{PPh}_3)(\text{S})(\text{S}_2\text{COMe})$ [23], the xanthate groups act as bidentate ligands and the mean Co–S bond lengths are, as expected, considerably shorter, viz. 2.277 and 2.269 Å, respectively.

Experimental

All manipulations were carried out under Ar or CO.

1. Preparation of $\text{PhSCo}(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ (**1a**)

a. From $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. In a Schlenk tube equipped with magnetic stirrer and dropping funnel, and connected to a gas burette, 238 mg (1 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 108 mg (2 mmol) of NaOMe were suspended and dissolved under CO in 5 ml of dry THF. First 236 mg (220 µl, 2.14 mmol) of PhSH were injected with a syringe, and then a solution of 713 mg (648 µl, 3.30 mmol) of PPh_2OMe in 5 ml of dry THF was added dropwise with constant stirring. During the addition the originally brown suspension turned into a deep red clear solution, and about 25 ml of CO was absorbed. After CO absorption had stopped the mixture was filtered, and the filtrate evaporated to dryness in vacuo. The residue was dissolved in 20 ml of diethyl

ether. Gradual cooling of this solution to -18°C yielded the product as orange crystals. Yield 210 mg (0.32 mmol), 32%. Found: C, 62.2; H, 5.3; Co, 8.7; P, 9.2; S, 4.9. $\text{C}_{34}\text{H}_{31}\text{CoO}_4\text{P}_2\text{S}$ calcd.: C, 62.20; H, 4.70; Co, 8.99; P, 9.45; S, 4.88%.

b. From $\text{Hg}[(\text{Co}(\text{CO})_2(\text{PPh}_2\text{OMe})_2)_2]$. In a Schlenk tube equipped with magnetic stirrer 356 mg (0.275 mmol) of $\text{Hg}[(\text{Co}(\text{CO})_2(\text{PPh}_2\text{OMe})_2)_2]$ and 126 mg (0.577 mmol) of Ph_2S_2 were dissolved under Ar in 10 ml of dry THF. After 1 h stirring the mixture was cooled to -10°C . Within 1 day the crystals of **1a** had separated, and were filtered off. Yield 138 mg (0.21 mmol), 38%.

2. Preparation of $\text{PhSCo}(\text{CO})_2(\text{PPh}_2^i\text{Bu})_2$ (**1b**)

This complex was prepared, but starting from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, by the method described for **1a**. Yield 266 mg (0.38 mmol), 38%. Found: C, 67.4; H, 6.2; Co, 8.5; P, 8.7; S, 4.3. $\text{C}_{40}\text{H}_{43}\text{CoO}_2\text{P}_2\text{S}$ calcd.: C, 67.60; H, 6.05; Co, 8.33; P, 8.75; S, 4.50%.

3. Preparation of $\text{MeOCS}_2\text{Co}(\text{CO})_2(\text{PPh}_2^i\text{Bu})_2 \cdot \text{MeCN}$ (**5** · *MeCN*)

In a Schlenk tube equipped with magnetic stirrer and dropping funnel, and connected to a gas burette 238 mg (1 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 527 mg (515 μl , 2.18 mmol) of PPh_2^iBu were dissolved under CO in 10 ml of MeOH. With constant stirring the solution of 292 mg (2 mmol) MeOCS_2K in 10 ml MeOH was added dropwise during 3 h; 26.4 ml of CO were absorbed. The mixture was evaporated to dryness in vacuo and the residue dissolved in THF. The solution was filtered and the filtrate again evaporated to dryness in vacuo. The residue was dissolved in 10 ml MeCN and the solution cooled to 5°C . The product separated as yellow-brown crystals. Yield 108 mg (0.145 mmol), 14.5%. Found: C, 61.2; H, 6.1; Co, 8.2; N, 1.8; P, 8.1; S, 8.5. $\text{C}_{38}\text{H}_{44}\text{CoO}_3\text{P}_2\text{S}_2$ calcd.: C, 61.12; H, 5.89; Co, 7.90; N, 1.87; P, 8.31; S, 8.58%.

4. Formation of $^i\text{BuPh}_2\text{PO}$

The solution obtained from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), PPh_2^iBu (1.03 mmol), NaOMe (1 mmol), PhSH (1.07 mmol), and 5 ml of THF under CO by the method described above (CO absorption 9 ml) was evaporated to dryness in vacuo and the residue dissolved in 10 ml hexane. Cooling of the vivid red solution to -15°C gave colorless crystals, which were identified by GC-MS as $^i\text{BuPh}_2\text{PO}$. Characteristic fragments in the order of decreasing intensity: 215, 258 (M^+), 201, 77.

5. X-ray structural determinations

Crystallographic data are given in Table 3. Specimens of **1a** and **5** were mounted on glass fibers. From the photographic evidence and systematic absences in the diffraction data, **1a** was found to be triclinic and the space group assumed to be $P\bar{1}$, and **5** monoclinic with space group $P2_1/c$. No absorption corrections were required but **5** was corrected for a 14% linear decay in intensity.

The structures were solved and completed by subsequent difference Fourier syntheses. In both cases, disordered, probably substoichiometric, small molecule sites were located, but no models could be constructed that led to chemical identification. They were arbitrarily refined as C atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. Terminal phenyl groups were constrained to rigid, planar hexagons.

Table 3

Crystallographic data for **1a** and **5**

	1a	5
<i>Crystal parameters</i>		
formula	$C_{34}H_{31}O_4P_2SCo \cdot S^a$	$C_{36}H_{41}O_3P_2S_2Co \cdot S^a$
space group	$P\bar{1}$	$P2_1/c$
crystal system	triclinic	monoclinic
a , Å	9.002(2)	12.051(3)
b , Å	10.291(2)	16.460(4)
c , Å	19.507(4)	19.858(5)
α , °	92.05(2)	—
β , °	99.99(2)	101.46(2)
γ , °	98.37(2)	—
V , Å ³	1757.3(6)	3860.4(2)
Z	2	4
cryst. dims., mm	0.25 × 0.25 × 0.30	0.21 × 0.32 × 0.51
cryst. color	orange	red
$D(\text{calc})$, g/cm ³	1.331	1.257
$\mu(\text{Mo-K}\alpha)$, cm ⁻¹	6.65	6.58
temp, °C	23	23
<i>Data collected</i>		
diffractometer	Nicolet R3m	
monochromator	graphite	
scan technique	Wyckoff	
radiation	Mo-K α ($\lambda = 0.71073$)	
2θ scan range, °	4–50	4–42
data collected	$\pm 11, \pm 13, +24$	$\pm 13, +17, +21$
rflns. collected	6497	4489
indpt. rflns.	6398	4144
$R(\text{merg})$, %	1.68	1.73
indpt. rflns. obsvd.	4100	2021
	$F_o > 5\sigma F_o$	$5\sigma F_o$
std. rflns.	3 std/197 rflns	3 std/197 rflns
var. in stds, %	<1	~14
$R(F)$, %	4.63	5.98
$R(wF)$, %	4.93	6.32
Δ/σ (max)	0.074	0.105
$\Delta(\rho)$, eÅ ⁻³	0.396	0.498
GOF	1.213	1.196
No/Nv	12.38	5.65

^a S = solvent. For **1a** and **5**, unresolvably disordered atom groups without obvious chemical interpretation were refined as C atoms. The occupancies are probably substoichiometric, and their contributions have not been included in the density calculations.

All software used in the solution and refinement were contained in the SHELXTL-5.1 program library (Nicolet XRD, Madison, WI).

Complete lists of bond lengths and angles, and lists of thermal parameters and structure factors are available from ALR.

References

- 1 S. Antebi and H. Alper, *Tetrahedron Lett.*, 26 (1985) 2609.
- 2 S. Antebi and H. Alper, *Organometallics*, 5 (1986) 596.

- 3 H. Alper and F. Sibtain, *J. Org. Chem.*, 53 (1986) 3306.
- 4 S.C. Shim, S. Antebi and H. Alper, *Tetrahedron Lett.*, 26 (1985) 1935.
- 5 S.C. Shim, S. Antebi and H. Alper, *J. Org. Chem.*, 50 (1985) 147.
- 6 H. Takahashi, K. Ohe, S. Uemura and N. Sugita, *J. Organomet. Chem.*, 334 (1987) C43.
- 7 S. Calet, H. Alper, J.-F. Petignani and H. Arzoumanian, *Organometallics*, 6 (1987) 1625.
- 8 M.-D. Wang, S. Calet and H. Alper, *J. Org. Chem.*, 54 (1989) 20.
- 9 E. Klumpp, L. Markó and G. Bor, *Chem. Ber.*, 97 (1964) 926.
- 10 L. Markó and G. Bor, *J. Organomet. Chem.*, 3 (1965) 162.
- 11 E. Klumpp, G. Bor and L. Markó, *Chem. Ber.*, 100 (1967) 1451.
- 12 C.H. Wei and L.F. Dahl, *J. Am. Chem. Soc.*, 90 (1968) 3960.
- 13 C.H. Wei and L.F. Dahl, *J. Am. Chem. Soc.*, 90 (1968) 3969.
- 14 C.H. Wei and L.F. Dahl, *J. Am. Chem. Soc.*, 90 (1968) 3977.
- 15 S.H. Wei and L. Markó, G. Bor and L.F. Dahl, *J. Am. Chem. Soc.*, 95 (1973) 4840.
- 16 L. Markó, *Gazz. Chim. Ital.*, 109 (1979) 247.
- 17 M. Tasi, P. Zani, G. Maccagnani and G. Pályi, *Z. Anorg. Allg. Chem.*, 581 (1990) 82.
- 18 W. Hieber and H. Duchatsch, *Chem. Ber.*, 98 (1965) 2530.
- 19 M. Bressan, B. Corain, P. Rigo and A. Turco, *Inorg. Chem.*, 9 (1970) 1733
- 20 C.C. Tso and A.R. Cutler, *Organometallics*, 5 (1986) 1834.
- 21 J. Newman and A.R. Manning, *J. Chem. Soc., Dalton Trans.*, (1972) 241.
- 22 M.E. Peach, *J. Inorg. Nucl. Chem.*, 41 (1979) 1390.
- 23 L. Markó, G. Gervasio, P.L. Stanghellini and G. Bor, *Transition Met. Chem.*, 10 (1985) 344.
- 24 D. Swenson, N.A. Baenzinger and D. Coucouvanis, *J. Am. Chem. Soc.*, 100 (1978) 1932.
- 25 I.G. Dance, *J. Am. Chem. Soc.*, 101 (1979) 6264.
- 26 D.T. Corwin, E.S. Gruff and S.A. Koch, *J. Chem. Soc., Chem. Commun.*, (1987) 966.
- 27 S. Merlino, *Acta Crystallogr., Sect B*, 25 (1969) 2270.