

Facile one-step synthesis of the cobalt(III) and nickel(III) tertiary arsine complexes $[Ml_3(AsMe_3)_2]$ ($M = Co$ or Ni) directly from the powdered elemental metals

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Diiodotrimethylarsine, Me_3AsI_2 , was treated with cobalt or nickel metal powder to give the metal(III) complex, $[Ml_3(AsMe_3)_2]$. In the case of cobalt, a metal(II) complex, $[AsMe_3I][CoI_3(AsMe_3)]$, was also produced, whereas for the nickel reaction only the nickel(III) complex, $[NiI_3(AsMe_3)_2]$, was formed in quantitative yield. The only other product from the reactions was diiodine, which was detected spectrophotometrically. Both complexes have been crystallographically characterised and found to be isostructural, consisting of a metal(III) atom with three equatorial iodide ligands capped by two trimethylarsine ligands. These complexes are unique examples of X-ray structural characterisation of compounds of this stoichiometry. Conventional wisdom would not have expected the 'soft' ligands I^- and $AsMe_3$ to bind to the relatively hard metal(III) centre.

The chemistry of cobalt and nickel complexes containing tertiary phosphine ligands has received considerable attention and is generally well understood.¹ Studies have, however, mainly been confined to cobalt and nickel tertiary phosphine complexes containing the metal in the dipositive oxidation state. Apart from pioneering work by Jensen,² complexes containing the metal in the tripositive oxidation state have only received worthwhile study recently. Levason and co-workers³⁻⁵ studied a series of $[MX_3(PR_3)_2]$ complexes ($R_3 = Me_3, Et_3, PhMe_2, PhEt_2$ or Ph_2Et ; $X = Cl$ or Br) and concluded from spectroscopic techniques that all such complexes are monomeric molecular trigonal-bipyramidal species with equatorial halide ligands capped by two tertiary phosphine ligands. These conclusions were in agreement with previous X-ray crystallographic studies on $[CoCl_3(PEt_3)_2]$ ⁶ (low precision) and $[NiI_3(PMe_3)_2]$,⁷ the latter being obtained serendipitously from the reaction of $[Ni(\mu-AsBu'_2)(PMe_3)_2]_2$ with diiodine.

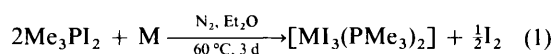
On the other hand, negligible work has been carried out on similar systems containing tertiary arsine ligands and no simple species of formula $[MX_3(AsMe_3)_2]$ ($M = Co$ or Ni) has received thorough attention. Moreover, no structural information is available for any complex of this stoichiometry.

Early reports have shown spectroscopically that tertiary arsine ligands form complexes with cobalt(II), the first reported example being $[CoI_2(AsPh_3)_2]$ by Cotton and co-workers.⁸ Similarly, $[CoX_2(AsEt_3)_2]$ ($X = Cl, Br$ or I), have been spectroscopically characterised by Hatfield and Yoke.⁹ The first crystallographically characterised complex containing a cobalt(II) tertiary arsine bond, $[(Ph_3AsI)_2I][Co(AsPh_3)_3]$, has been reported only very recently and was prepared from the novel reaction of $[Co_2(CO)_8]$ with the oxidising agent Ph_3AsI_2 .¹⁰

Additionally, in the case of cobalt, four crystal structures containing cobalt(III) and tertiary arsine donors have been reported containing chelating ligands. $[CoCl_2\{C_6H_4(AsMe_2)_{2-o}\}_2]ClO_4$,¹¹ $[CoCl_2\{CH_2(CH_2AsMe_2)_2\}_2]ClO_4$,¹² $[Co\{C_6H_4(AsMe_3)_{2\}o\}_3][(BF_3)_3\cdot H_2O]$ ¹³ and a cobalt(III) complex of an As_2PN donor ligand.¹⁴ Levason and Preece¹⁵ have recently reported a spectroscopic and extended X-ray absorption fine structure (EXAFS) study of some nickel(III) complexes containing chelating tertiary arsine ligands of formula $[Ni-$

$\{C_6H_4(AsMe_2)_{2-o}\}_2I_2]BF_4$ and $[Ni\{C_6F_4(AsMe_2)_{2-o}\}_2I_2]BF_4$, from which it was concluded that in these $3d^7$ complexes the nickel(III) moiety had a tetragonally distorted environment. It was also noted that attempts to grow single crystals from the nickel(III) solutions were unsuccessful. The EXAFS data gave the Ni-As bond length as *ca.* 2.35 Å and the Ni-I bond length as *ca.* 2.73 Å. Thus, prior to this work, no cobalt(III) or nickel(III) complex containing only halide and monodentate tertiary arsine ligands had been X-ray crystallographically characterised.

We have previously reported a wide range of reactions of the novel oxidising agents R_3EX_2 ($E = P, As$ or Sb ; $X = Br$ or I) with coarse-grain unactivated metal powders. We have found that such reagents provide a method of synthesising metal complexes containing the metal in a high oxidation state.¹⁶⁻¹⁸ For example, the reaction of nickel or cobalt metal powder with Me_3PI_2 produces the M^{III} complex in quantitative yield in a simple one-step reaction,¹⁸ equation (1). We have also



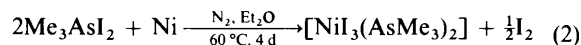
illustrated that this novel reaction route can produce complexes which defy the normal HSAB (hard and soft acid and base) principle. For example, the reaction of Ph_3SbI_2 with cobalt metal powder produces both $[SbPh_3I][CoI_3(SbPh_3)]$ ¹⁶ and $[CoI_3(SbPh_3)_2]$.¹⁹ The latter is the only example of a cobalt(III) complex containing the 'soft' iodide and antimony donors and would not previously have been thought to be capable of existence. More recently, we have extended our studies to investigate the reaction of certain R_3EX_2 compounds ($E = P, As$ or Sb ; $X_2 = Br_2, I_2$ or IBr) with metal(0) carbonyl systems. For example, 6 equivalents of Ph_3AsI_2 reacts with $[Co_2(CO)_8]$ to produce $[(AsPh_3I)_2I][CoI_3(AsPh_3)]$, a complex containing the unusual linear $[Ph_3As-I-I-I-AsPh_3]^+$ cation.¹⁰

In view of these results, and the extreme paucity of reports concerning M^{III} ($M = Co$ or Ni) complexes containing tertiary arsine donors we decided to investigate the reaction of Me_3AsI_2 with cobalt and nickel metal powders. Since cobalt(III) and nickel(III) are both hard acceptors and iodide and tertiary arsine ligands are soft donors, the reactions provide the opportunity to

characterise further examples of metal complexes which appear to defy the HSAB principle.

Results and Discussion

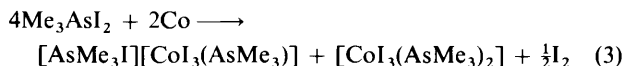
Diiodotrimethylarsine, Me_3AsI_2 , reacts with nickel metal powder according to equation (2). The synthesis and structural



characterisation of Me_3AsI_2 has been described elsewhere.²⁰ Interestingly, Me_3AsI_2 reacts with nickel metal powder to produce the metal(III) complex $[\text{NiI}_3(\text{AsMe}_3)_2]$ in quantitative yield, which is directly analogous to the reaction of Me_3PI_2 with nickel metal powder to produce $[\text{NiI}_3(\text{PMe}_3)_2]$,¹⁸ and the diiodine produced in solution was quantitatively detected spectrophotometrically. The complex is paramagnetic, exhibiting $\mu_{\text{eff}} = 1.94 \mu_{\text{B}}$ ($\mu_{\text{B}} \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$). Recrystallisation of the magenta powder from diethyl ether produced dark purple crystals suitable for analysis by single-crystal X-ray diffraction; the crystal structure of $[\text{NiI}_3(\text{AsMe}_3)_2]$ is illustrated in Fig. 1. The molecule is trigonal bipyramidal with axial tertiary arsine ligands; thus, $[\text{NiI}_3(\text{AsMe}_3)_2]$ represents the first complex of this formula to be crystallographically characterised. Selected bond lengths and angles and fractional atomic coordinates for the complex are displayed in Tables 1 and 2, respectively. Surprisingly, $[\text{NiI}_3(\text{AsMe}_3)_2]$ is quite stable both in the solid state and in dry diethyl ether. The complex appears to be indefinitely stable when stored in an inert atmosphere at room temperature and stable for several hours in diethyl ether exposed for several hours to the atmosphere. The electronic spectrum of $[\text{NiI}_3(\text{AsMe}_3)_2]$ in diethyl ether exhibits two bands at 541 and 648 nm.

Venanzi and Norgett²¹ devised a one-electron transition scheme for the d^7 trigonal-bipyramidal nickel(III) system; however, the assignment of bands with high absorption coefficients in nickel(III) complexes as d-d bands has been questioned by Levason and co-workers²² since other weaker bands were observed in the near infrared which are more likely to be due to d-d transitions. Consequently, the two bands at 541.0 and 648.5 nm in the spectrum of $[\text{NiI}_3(\text{AsMe}_3)_2]$ are probably due to $\text{P}(\sigma) \rightarrow \text{Ni}(a_1)$ and $\text{P}(\sigma) \rightarrow \text{Ni}(e_a^1)$ charge-transfer transitions, respectively. The position of the bands and the absorption coefficient for the transition at 541.0 nm ($9920 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) is similar to that previously recorded for $[\text{NiI}_3(\text{PMe}_3)_2]$,¹⁷ as expected, since $[\text{NiI}_3(\text{AsMe}_3)_2]$ and $[\text{NiI}_3(\text{PMe}_3)_2]$ are isostructural. Additionally, the profile of the electronic spectrum and the absorption coefficients are similar to analogous $[\text{NiX}_3(\text{PR}_3)_2]$ complexes prepared by Levason and co-workers.^{3,22}

On the other hand, the reaction of cobalt metal powder with Me_3AsI_2 produces both a cobalt(II) and a cobalt(III) complex [equation (3)]. The cobalt(III) complex, $[\text{CoI}_3(\text{AsMe}_3)_2]$, was



obtained in 60% yield. Although this result is surprising, it is not without precedent. We have previously reported that the reaction of Me_3PI_2 with cobalt powder produces the dark green cobalt(III) complex, $[\text{CoI}_3(\text{PMe}_3)_2]$, in quantitative yield,¹⁶ but the reaction of PhMe_2PI_2 with cobalt powder produces both the cobalt(III) complex $[\text{CoI}_3(\text{PPhMe}_2)_2]$ and the cobalt(II) complex $[\text{PPhMe}_2\text{I}][\text{CoI}_3(\text{PPhMe}_2)]$. Moreover, the reaction of Et_3PI_2 with cobalt powder produced only the cobalt(II) complex, $[\text{PEt}_3\text{I}][\text{CoI}_3(\text{PEt}_3)]$, in quantitative yield.¹⁷ This is surprising, since the basicity of trimethylphosphine ($\text{p}K_{\text{a}} 8.65$) and triethylphosphine ($\text{p}K_{\text{a}} 8.69$) are virtually identical, suggesting that the basicity of the tertiary phosphine is

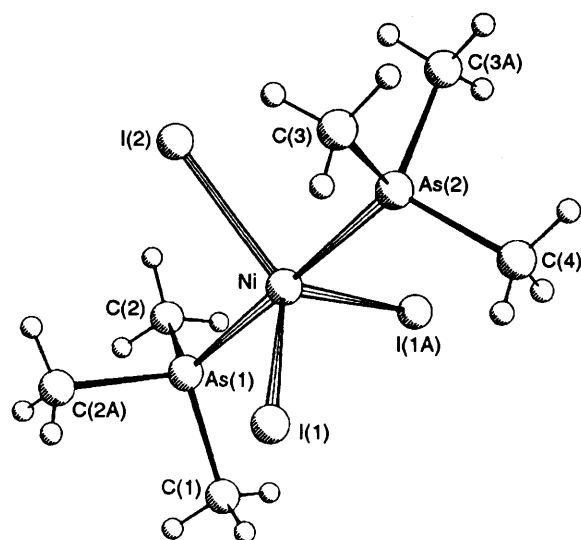


Fig. 1 Crystal structure of $[\text{NiI}_3(\text{AsMe}_3)_2]$

Table 1 Selected bond lengths (Å) and angles (°) for $[\text{NiI}_3(\text{AsMe}_3)_2]$

Ni–I(1)	2.550(5)	As(1)–C(1)	1.92(6)
Ni–I(2)	2.531(9)	As(1)–C(2)	1.91(4)
As(1)–Ni	2.32(1)	As(1)–C(2)	1.96(4)
As(2)–Ni	2.35(1)	As(2)–C(4)	1.89(5)
Ni–As(1)–C(1)	117(2)	I(1)–Ni–I(1)	114.7(3)
Ni–As(1)–C(2)	115(1)	I(1)–Ni–I(2)	122.6(1)
C(1)–As(1)–C(2)	104(1)	I(1)–Ni–As(1)	90.4(2)
Ni–As(2)–C(3)	115(1)	I(2)–Ni–As(1)	90.7(3)
Ni–As(2)–C(4)	114(2)	As(1)–Ni–As(2)	179.9(4)
C(3)–As(2)–C(4)	105(1)		

Table 2 Fractional atomic coordinates for the non-hydrogen atoms in $[\text{NiI}_3(\text{AsMe}_3)_2]$

Atom	x	y	z
I(1)	0.8949(3)	0.0610(3)	0.5971(2)
I(2)	0.5359(4)	$\frac{1}{4}$	0.3929(3)
As(1)	0.8694(6)	$\frac{1}{4}$	0.4191(5)
As(2)	0.5259(6)	$\frac{1}{4}$	0.6302(4)
Ni	0.6988(7)	$\frac{1}{4}$	0.5342(5)
C(1)	1.042(6)	$\frac{1}{4}$	0.470(4)
C(2)	0.870(4)	0.379(4)	0.334(3)
C(3)	0.406(3)	0.117(4)	0.618(3)
C(4)	0.578(5)	$\frac{1}{4}$	0.755(4)

unimportant in determining whether a cobalt(II) or -(III) species is formed. Additionally, the basicity of trimethylarsine is considerably lower than triethylphosphine, but the reaction of Me_3AsI_2 with cobalt metal powder still produces some cobalt(III) complex, $[\text{CoI}_3(\text{AsMe}_3)_2]$. If we examine the cone angles of the tertiary phosphines, trimethylphosphine (118°), dimethylphenylphosphine (122°) and trimethylarsine (121°), the values are very similar, whereas the cone angle for triethylphosphine (132°) is appreciably larger.²³ Therefore, it may be steric factors which determine whether a cobalt(II) or -(III) species is produced, although we cannot suggest why. Presumably the reaction of the R_3EI_2 species ($\text{R}_3 = \text{Me}_3$, Et_3 or PhMe_2 , $\text{E} = \text{P}$; $\text{R} = \text{Me}$; $\text{E} = \text{As}$) with the cobalt metal powder involves an intermediate where steric factors are important. We are currently investigating the mechanism of this new reaction to determine whether this is the case.

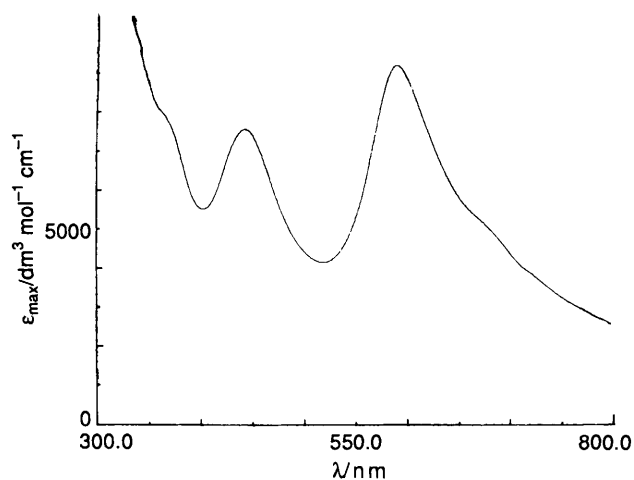
Recrystallisation of the dark green powder from diethyl ether produced dark green-black crystals on standing at 0°C ; one was selected for single-crystal X-ray analysis and $[\text{CoI}_3(\text{AsMe}_3)_2]$ is found to be isostructural with the nickel(III)

Table 3 Selected bond lengths (Å) and angles (°) for $[\text{CoI}_3(\text{AsMe}_3)_2]$

I(1)–Co	2.510(5)	As(1)–C(2)	1.87(3)
I(2)–Co	2.530(3)	As(2)–Co	2.327(6)
As(1)–Co	2.340(6)	As(2)–C(3)	1.88(3)
As(1)–C(1)	1.93(4)	As(2)–C(4)	1.86(4)
Co–As(1)–C(1)	117(1)	I(1)–Co–I(2)	120.8(1)
Co–As(1)–C(2)	115.4(7)	I(1)–Co–As(1)	89.9(2)
C(1)–As(1)–C(2)	101(1)	I(2)–Co–I(2)	118.4(2)
Co–As(2)–C(3)	114.6(9)	I(2)–Co–As(1)	90.6(2)
Co–As(2)–C(4)	116(1)	As(1)–Co–As(2)	†78.9(3)
C(3)–As(2)–C(4)	103(1)		

Table 4 Fractional atomic coordinates for the non-hydrogen atoms in $[\text{CoI}_3(\text{AsMe}_3)_2]$

Atom	x	y	z
I(1)	0.5351(3)	$\frac{1}{4}$	0.3948(2)
I(2)	0.7791(2)	0.0562(2)	0.5971(1)
As(1)	0.7813(5)	$\frac{1}{4}$	0.4201(2)
As(2)	0.5213(4)	$\frac{1}{4}$	0.6321(2)
Co	0.6972(5)	$\frac{1}{4}$	0.5276(3)
C(1)	1.048(4)	$\frac{1}{4}$	0.470(2)
C(2)	0.877(2)	0.381(2)	0.339(2)
C(3)	0.409(3)	0.117(3)	0.623(2)
C(4)	0.566(4)	$\frac{1}{4}$	0.758

**Fig. 2** Electronic spectrum of $[\text{CoI}_3(\text{AsMe}_3)_2]$ in diethyl ether

complex illustrated in Fig. 1. Selected bond lengths and angles and fractional atomic coordinates for the non-hydrogen atoms are displayed in Tables 3 and 4, respectively. The $[\text{CoI}_3(\text{AsMe}_3)_2]$ complex is trigonal bipyramidal with equatorial iodide ligands and represents the first structurally characterised complex of this stoichiometry and the first cobalt(III) complex reported containing monodentate tertiary arsine donor ligands. The electronic spectrum of $[\text{CoI}_3(\text{AsMe}_3)_2]$ in diethyl ether is illustrated in Fig. 2. The spectrum shows two intense bands, one at 460 ($\epsilon_{\text{max}} = 7200$) and the other at 592 nm ($\epsilon_{\text{max}} = 9280 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Both bands are probably due to ligand-to-metal charge-transfer transitions, $\lambda = 460$, $\text{I}(\pi) \rightarrow e^1$, $\lambda = 592$ nm, $\text{As}(\sigma) \rightarrow e^1$. The appearance of the spectra and the intensity of the transitions are very similar to those of $[\text{CoI}_3(\text{PMe}_3)_2]$ prepared by us,¹⁶ and other cobalt(III) tertiary arsine complexes prepared by Levason and co-workers.⁴ Attempts to record the $^{13}\text{C}\{-\text{H}\}$ NMR spectrum of $[\text{CoI}_3(\text{AsMe}_3)_2]$ resulted only in a broad hump in a very noisy spectrum, analogous to our observations when we attempted to record the $^{31}\text{P}\{-\text{H}\}$ NMR spectrum of $[\text{CoI}_3(\text{PMe}_3)_2]$.¹⁶ Surprisingly, $[\text{CoI}_3(\text{AsMe}_3)_2]$ is relatively stable to air and moisture, only decomposing after ca. 1 week on exposure to atmospheric conditions.

More importantly, the facile oxidation of elemental cobalt and nickel by Me_3AsI_2 has been demonstrated. This novel oxidising agent is capable of oxidising the metals directly to the +3 oxidation state in a facile one-step reaction which does not require the use of any other oxidising agent. It is important to note that Levason and Spicer⁵ reported that attempts to oxidise cobalt(II) arsine complexes $[\text{CoX}_2(\text{AsEt}_3)_2]$ ($\text{X} = \text{Cl}$ or Br) with NOX ($\text{X} = \text{Cl}$ or Br) resulted in the decomposition of the complex; and therefore the synthesis of $[\text{CoI}_3(\text{AsMe}_3)_2]$ described here must be directly attributable to this new synthetic method. Clearly the reaction of R_3EX_2 species ($\text{E} = \text{P}$, As or Sb ; $\text{X} = \text{Br}$ or I) with metal powders provides a facile route to a large number of complexes, especially those containing the metal in high oxidation state, some of which would not have been thought of as capable of existence and may not be available from conventional synthetic techniques.

Experimental

Both of the complexes described are moisture sensitive, and strictly anaerobic and anhydrous conditions were adhered to during their synthesis. The synthesis of Me_3AsI_2 has been described elsewhere.²⁰ Diethyl ether was obtained from BDH, dried over sodium wire for ca. 1 d and then distilled over CaH_2 in an inert atmosphere prior to use; it was then distilled directly into the reaction vessel and degassed by passing nitrogen through for ca. 10 min. Standard-reagent-grade coarse-grain cobalt and nickel metal powders were obtained from Aldrich and used as received. After isolation, any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box.

The same reaction technique was employed for the synthesis of both $[\text{CoI}_3(\text{AsMe}_3)_2]$ and $[\text{NiI}_3(\text{AsMe}_3)_2]$, namely diiodotrimethylarsine (0.621 g, 1.66 mmol) was suspended in diethyl ether (ca. 100 cm^3) and subsequently either cobalt or nickel metal powder (0.049 g, 0.83 mmol) was added. After ca. 4 d the resultant solid was isolated by standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried argon-filled ampoules which were subsequently flame sealed. Both complexes gave satisfactory elemental analyses [Found (Calc.): for $\text{C}_6\text{H}_9\text{As}_2\text{CoI}_3$ C, 9.9 (10.6); H, 2.8 (2.6); I, 55.9 (56.0); for $\text{C}_6\text{H}_9\text{As}_2\text{I}_3\text{Ni}$ C, 10.2 (10.6); H, 2.9 (2.6); I, 55.7 (56.0)%].

Elemental analyses were performed by the analytical laboratory of this department. Electronic spectra were recorded in diethyl ether on a Shimadzu UV-2101PC spectrophotometer. Absorption coefficients were calculated by metal atomic absorption analysis of the solution to determine the amount of complex dissolved.

X-Ray crystallography

Crystals of both samples were mounted in Lindeman tubes under dry-box conditions (argon). All measurements were performed on a Rigaku AFC6S diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation. Crystal data and details of the refinement are presented in Table 5. Lorentz, polarisation and absorption corrections were applied {azimuthal scans: minimum, maximum transmission factors 0.88, 1.19 and 0.38, 1.00 for $[\text{CoI}_3(\text{AsMe}_3)_2]$ and $[\text{NiI}_3(\text{AsMe}_3)_2]$, respectively}. Both structures were solved by direct methods,²⁴ the heavy atoms were refined anisotropically and the hydrogen atoms were confined to chemically reasonable positions. Neutral-atom scattering factors were taken from ref. 25(a). Anomalous dispersion effects were included in F_o ; the values for $\Delta f'$ and $\Delta f''$ were taken from ref. 25(b). All calculations were performed using the TEXSAN-TEXRAY crystallographic software package.²⁶

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge

Table 5 Crystal data and details of refinement for $[Ml_3(AsMe_3)_2]$ ($M = Co$ or Ni)*

	$[CoI_3(AsMe_3)_2]$	$[NiI_3(AsMe_3)_2]$
M	679.70	679.46
Crystal size/mm	$0.30 \times 0.20 \times 0.05$	$0.30 \times 0.15 \times 0.10$
$a/\text{\AA}$	10.142(3)	10.298(5)
$b/\text{\AA}$	11.210(3)	11.363(3)
$c/\text{\AA}$	14.291(4)	14.440(5)
$U/\text{\AA}$	1625(1)	1690(2)
$D_c/g\text{ cm}^{-3}$	2.778	2.671
$F(000)$	1224	1228
μ/cm^{-1}	107.00	104.29
T/K	233	293
Total data measured	2699	1733
Maximum $2\theta/^\circ$	51.2	49.9
No. observed reflections [$I > 3.00\sigma(I)$]	726	397
Minimum, maximum $\rho/e\text{ \AA}^{-3}$	-1.75, 1.81	-1.36, 1.10
Maximum least-squares shift-to-error ratio	0.07	0.04
Final R'	0.068	0.055
Final R	0.070	0.058

* Details common to both refinements: orthorhombic, space group $Pnma$ (no. 62), $Z = 4$; 64 parameters; weighting scheme used $w = 1/[\sigma^2(F) + 0.03F^2]$; $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$; $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

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