Inorganica Chimica Acta, *217* (1994) 171–179

Synthesis and characterization of symmetric and unsymmetric oxo-bridged trinuclear chromium benzoate complexes: crystal and molecular structure of $[Cr_3O(O_2CPh)_6(py)_3]ClO_4$

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(Received July 28, 1993; revised November 17, 1993)

Abstract

Techniques have been developed for the synthesis of complexes of the type $[Cr_3O(O_2CR)_6(L)_3]^+$ where R = phenyl or tolyl and L = H_2O or py in non-aqueous solvents. Additionally, the synthesis of an unsymmetric trinuclear complex, $[Cr_3O(O_2CPh)_6(OH)(py)_2]$, is reported. These complexes have been characterized by a number of spectroscopic and magnetic techniques including X-ray crystallography, electronic and infrared spectrophotometry, NMR and EPR spectroscopy, mass spectrometry, and solution and solid state susceptibility measurements. $[Cr_3O(O_2CPh)_6(py)_3]ClO_4$ crystallizes in the hexagonal space group $P\bar{6}$, which has $a = 13.387(4)$, $c = 19.186(6)$ Å and $Z = 2$. The structure was refined to give $R = 7.6$ and $R_w = 10.1$.

Key words: Crystal structures; Chromium complexes; Oxo complexes; Carboxylate complexes, Trinuclear complexes

Introduction**

Trinuclear oxo-centered metal carboxylate assemblies of the general composition $[M_3O(O_2CR)_6L_3]^{n+}$ have been of intense interest for several decades, even before the first structure determination by X-ray diffraction in 1965 [1]. The importance of this class of compounds draws from many areas, as emphasized by the appearance of a recent review article [2]. These compounds serve as important models to test theories of magnetic coupling between metal ions in multinuclear systems [3–8] and as precursors to larger multinuclear assemblies whose novel magnetic properties are only now being realized [9–12]. The use of these complexes as precursors to larger assemblies has been limited primarily to Mn and Fe (see however refs. 13 and 14), where the solubility of the complexes of these metal ions in non-aqueous solvents has been utilized to prevent complications due to hydrolysis. To date, the synthesis of these assemblies where M = Cr(III) have been performed almost solely in water, which limits the accessible range of carboxylate ligands which can be utilized.

Reports of unsymmetric members of this class of compounds are rare [2]; for M = Cr(III), reports are limited to a few examples characterized only by elemental analysis prior to 1930 [15–17]. Herein are reported the synthesis and characterization of symmetric and unsymmetric oxo-centered chromium(III) benzoate assemblies.

Experimental

Syntheses

Reagents were obtained commercially and used as received. $[Cr_3O(O_2CPh)_6(py)_3]ClO_4$ (**1**) [18] and $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ [19] and their deuterio analogues were prepared as previously described. Other compounds containing deuterium-labelled ligands were prepared in analogous fashions to the protio analogues substituting $DO_2CC_5D_5$, D_2O or NC_5D_5 as required.

Caution: Appropriate care should be taken whenever perchlorate salts are heated.

$[Cr_3O(O_2CPh)_6(py)_3]Cl$ (2) $\cdot\frac{3}{4}CH_2Cl_2\cdot 3H_2O$

A mixture of 10.87 g $CrCl_3\cdot 6H_2O$ (40.79 mmol) and 12.20 g HO_2CPh (99.9 mmol) was stirred in 100 ml pyridine, heated to reflux for 4 h, allowed to cool to

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**NMR, Nuclear magnetic resonance; ESR, electron spin resonance; py, pyridine; *p*-tol, *para*-toluate; DMF, dimethylformamide; 4-CNpy, 4-cyanopyridine.

SSDI 0020-1693(93)03766-4

room temperature, and then filtered to reveal a green microcrystalline solid. The product was washed copiously with Et_2O and dried *in vacuo*. Yield *c*. 55% based on Cr. Recrystallization can be accomplished from CH_2Cl_2/hexane. *Anal*. Found: C, 54.09; H, 4.23; N, 3.22; Cl, 7.40; Cr, 12.32. Calc. for $Cr_3O_{16}C_{57.75}H_{52.5}N_3Cl_{2.5}$: C, 53.80; H, 4.10; N, 3.26; Cl, 6.87; Cr, 12.10%. IR: 1615(vs), 1580(s), 1225(m), 1185(w), 1170(s), 1080(m), 1050(w), 1020(m), 755(s), 720(s), 700(vs), 640(vs), 515(vs) cm^{-1}.

*$[Cr_3O(p\text{-tol})_6(py)_3]ClO_4$ (**3**) $\cdot 1.8CH_2Cl_2$*

A mixture of 18.70 g $Cr(ClO_4)_3 \cdot 6H_2O$ (40.79 mmol) and 12.20 g *p*-toluic acid (89.61 mmol) was refluxed for 4 h in 100 ml pyridine, allowed to cool, stored at 4 °C overnight and filtered. The green solid was washed copiously with Et_2O and dried *in vacuo*. Yield *c*. 70% based on Cr. Recrystallization was accomplished from CH_2Cl_2/hexanes. *Anal*. Found: C, 52.35; H, 3.96; N, 2.75; Cl, 10.27; Cr, 10.70. Calc. for $Cr_3O_{17}H_{60.6}C_{64.8}N_3Cl_{4.6}$: C, 52.86; H, 4.15; N, 2.85; Cl, 11.07; Cr, 10.59%. IR: 1620(vs), 1580(s), 1305(w), 1275(m), 1250(w), 1230(m), 1190(s), 1170(m), 1090(vs), 1050(m), 1025(m), 955(w), 850(s), 765(vs), 740(s), 700(vs), 660(s), 640(s), 625(vs), 510(s), 495(s), 485(s) cm^{-1}.

*$[Cr_3O(O_2CPh)_6(H_2O)_3]NO_3$ (**4**) $\cdot H_2O$*

A mixture of 16.00 g $Cr(NO_3)_3 \cdot 9H_2O$ (40.0 mmol) and 9.76 g benzoic acid (80.0 mmol) was stirred in 120 ml EtOH, refluxed for $2\frac{1}{2}$ h, allowed to cool to room temperature, stored overnight at *c*. −20 °C and filtered. The blue–green microcrystalline solid was washed copiously with Et_2O and dried *in vacuo*. Yield *c*. 57% based on Cr. Recrystallization was accomplished from MeCN. *Anal*. Found: C, 49.17; H, 3.59; Cr, 15.07. Calc. for $Cr_3O_{20}C_{42}H_{38}N$: C, 48.84; H, 3.71; Cr, 15.10%. IR: 1625(vs), 1580(vs), 1300(s), 1180(m), 1165(m), 1075(w), 1025(m), 940(w), 850(w), 815(w), 720(vs), 680(sh), 660(vs), 620(sh), 520(vs) cm^{-1}.

*$[Cr_3O(O_2CPh)_6(H_2O)_3]ClO_4$ (**5**) $\cdot 1.1CCl_4 \cdot 2H_2O$*

3.51 g $Cr(ClO_4)_3 \cdot 6H_2O$ (7.66 mmol) and 4.88 g benzoic acid (40.0 mmol) were dissolved in 50 ml MeCN to give a blue–purple solution. After refluxing 4 h, the resulting turquoise-colored solution was allowed to cool and stored overnight at *c*. 4 °C. After filtering to remove precipitated benzoic acid, the solution was striped to dryness under vacuum. The solid was extracted with 30 ml deionized water and filtered. The blue filtrate was discarded, and the solid was extracted with 60 ml CCl_4 to remove excess benzoic acid. The mixture was filtered; extracting the solid with 15 ml acetone gave a deep green solution. Allowing the solution to concentrate gave green crystals which were filtered, washed copiously with CCl_4, and dried thoroughly *in vacuo*. Yield *c*. 10% based on Cr. *Anal*. Found: C, 46.03; H, 3.55; Cl, 3.79; Cr, 13.99. Calc. for $Cr_3O_{22}Cl_{1.25}C_{42.0625}H_{40}$: C, 46.02; H, 3.67; Cl, 4.04; Cr, 14.2%. IR: 3450(br, vs), 1630(vs), 1585(s), 1320(m), 1295(w), 1250(w), 1190(m), 1090(vs), 1030(m), 940(w), 850(w), 820(w), 790(w), 720(vs), 685(s), 625(s), 525(vs) cm^{-1}.

*$[Cr_3O(O_2CPh)_6(py)_2(OH)]$ (**6**) $\cdot H_2O$*

A mixture of 10.87 g $CrCl_3 \cdot 6H_2O$ (40.8 mmol) and 12.20 g HO_2CPh (99.9 mmol) was stirred in 100 ml pyridine, heated to reflux for 4 h, allowed to cool to room temperature, and filtered. The solid was washed copiously with Et_2O. The dried solid was refluxed in 40 ml MeCN for 3 h. The mixture was allowed to cool and was then filtered. The resulting green solid was washed with Et_2O and dried *in vacuo*. Yield *c*. 35% based on Cr. *Anal*. Found: C, 57.30; N, 2.19; H, 4.18. Calc. for $Cr_3C_{52}H_{40}N_3$: C, 57.19; N, 2.57; H, 3.97%. IR: 1625(vs), 1585(vs), 1320(w), 1225(m), 1185(m), 1165(m), 1075(m), 1050(m), 1025(m), 940(w), 845(w), 815(w), 760(m), 720(vs), 700(s), 680(s), 650(sh), 645(s), 600(sh), 515(vs) cm^{-1}.

Instrumental methods

^1H and ^2H NMR spectra were obtained using a Bruker AM-360 and a Bruker AM-500 spectrometer, respectively at *c*. 25 °C. Chemical shifts are reported on the δ scale (shifts downfield are positive) using the solvent protio- or deutero- impurity signal(s) as reference. Assignments were made on the basis of relative intensities and broadening and by substitution of appropriate ligands [18]. IR spectra (as nujol mulls) were recorded using a Perkin-Elmer 283B spectrophotometer. A Hewlett-Packard 8451A spectrophotometer was used to obtain UV–Vis spectra. Fast atom bombardment mass spectra were obtained using a VG Autospec high resolution mass spectrometer. Solution susceptibility measurements were acquired using the Evan's NMR method [20], employing hexamethyldisiloxane as the reference peak; solid state susceptibilities were acquired using a Johnson-Matthey susceptibility balance. Diamagnetic corrections were employed using Pascal's constants. ESR spectra were collected on a Varian E-12 spectrophotometer equipped with an Oxford ESR 900 cryostat.

X-ray crystallography

Single crystals of $[Cr_3O(O_2CPh)_6(py)_3]ClO_4$ (**1**) were sealed in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of the angular settings of 24 high angle reflections ($2\theta > 30°$) accurately centered on an Enraf-Nonius CAD4 diffractometer are given in Table 1. Data were collected by the θ–2θ scan techniques as described in the literature [21]. The intensities were corrected for

TABLE 1. Crystallographic data for $[Cr_3O(O_2CPh)_6(py)_3]ClO_4$ (1)

Formula	$Cr_3C_{57}H_{45}O_{17}N_3Cl$
Molecular weight	1235 44
Space group	$P\bar{6}$
a (Å)	13.387(4)
b (Å)	13 387(4)
c (Å)	19 186(6)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	2978
Z	2
ρ_{calc} (g cm^3)	1.383
μ (cm^{-1})	6.39
Radiation	Mo Kα
R	0.076
R_w	0.101

Lorentz and polarization effects, and an empirical absorption correction based on psi scan data was performed. Calculations were carried out using the SHELX system of computer programs [22].

Structural solution was accomplished with the aid of the direct methods program SHELX86 [23]. All non-hydrogen atoms were refined with anisotropic thermal parameters except atoms (01), (011) and C1). Hydrogen atoms were placed at calculated positions. Hydrogen atom parameters were not refined. Refinement converged with $R = 0.076$ for 2723 observed reflections. The final fractional coordinates are given in Table 2. Relevant bond lengths and angles are given in Table 3.

Results and discussion

Synthesis and structures

In general, oxo-centered chromium(III) trimers have been prepared by the reaction of carboxylic acids with freshly prepared chromium(III) hydroxide [2, 19, 24, 25, and refs. therein] or oxidation of chromium(II) acetate (unstable to air) by ozone or an ozone/air mixture [25, 26]. By allowing the reaction mixtures to evaporate, green oils or syrupy solids result which are probably comprised of a polymeric array of these trinuclear units bridged by carboxylates. Recrystallization in the presence of anions or mineral acids and a terminal ligand L (usually pyridine or water) gives species of the formula $[Cr_3O(O_2CR)_6(L)_3]X$, where X is a monoanion. However, as demonstrated herein these trimers can be synthesized in one pot reactions in high yield using a variety of commercially available, inexpensive chromium(III) salts, carboxylic acids, and non-aqueous solvents. This reaction is summarized in eqn. (1).

TABLE 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) with e.s.d.s in parentheses

Atom	x/a	y/b	z/c	U_{eq}
Cr(1)	0.5120(4)	0.2992	0.5000	0.30(6)
O(1)	0.6666	0.3333	0.5000	0.038(8)
O(2)	0.464(1)	0.184(1)	0.4231(7)	0.038(4)
O(3)	0.531(1)	0.417(1)	0.4323(8)	0.024(8)
C(1)	0.494(1)	0.112(1)	0.4057(7)	0.017(8)
C(2)	0.428(2)	0.025(2)	0 359(1)	0.048(3)
C(3)	0.325(2)	0.010(2)	0 325(1)	0.048(8)
C(4)	0.261(2)	−0.067(2)	0 285(1)	0.073(7)
C(5)	0.292(2)	−0.152(2)	0.260(1)	0.079(29)
C(6)	0.395(2)	−0.147(2)	0.293(2)	0.093(65)
C(7)	0.447(2)	−0.070(2)	0.341(1)	0.063(24)
N(A1)	0.325(2)	0.252(2)	0.5000	0.057(47)
C(A1)	0.284(2)	0.246(2)	0.439(1)	0.042(12)
C(A2)	0.173(2)	0.227(3)	0.447(2)	0.091(35)
C(A3)	0.106(4)	0.217(4)	0.5000	0.085(22)
Cr(2)	0.212(3)	0.5098(4)	0.0000	0.030(3)
O(11)	0.3333	0.6667	0.0000	0.028(8)
O(21)	0.126(1)	0.523(1)	0.0755(6)	0.040(16)
O(31)	0.285(1)	0.459(1)	0.0678(8)	0.046(8)
C(11)	0.117(2)	0.608(2)	0.086(1)	0.063(37)
C(21)	0.18(1)	0.593(2)	0.143(1)	0.037(15)
C(31)	−0.053(2)	0.480(2)	0.162(1)	0.046(16)
C(41)	−0.135(2)	0.471(2)	0 211(1)	0.051(8)
C(51)	−0.137(2)	0.558(3)	0 243(1)	0.074(26)
C(61)	−0.068(2)	0.663(2)	0.227(1)	0.058(5)
C(71)	0.021(2)	0.686(2)	0.70(1)	0.038(13)
N(B1)	0.081(2)	0.343(2)	0.0000	0.026(5)
C(B1)	0.027(2)	0.271(2)	0.062(1)	0.076(13)
C(B2)	−0.051(1)	0.158(2)	0.066(1)	0.060(14)
C(B3)	−0.087(3)	0.111(2)	0.0000	0.078(70)

TABLE 3. Relevant bond lengths (Å) and angles (°)

Bond distances			
Cr(1)–N(A1)	2.245(2)	Cr(2)–N(B1)	2 04(2)
Cr(1)–O(1)	1.883(4)	Cr(2)–O(11)	1.903(4)
Cr(1)–O(2)	2.00(1)	Cr(2)–O(21)	1.96(1)
Cr(1)–O(3)	1.96(2)	Cr(2)–O(31)	1.94(1)
Cr(1)–Cr(1)′	3.263(8)	Cr(2)–Cr(2)′	3.295(8)
Bond angles			
N(A1)–Cr(1)–O(1)	178.1(6)	N(B1)–Cr(2)–O(11)	178.3(6)
N(A1)–Cr(1)–O(2)	84.3(5)	N(B1)–Cr(2)–O(21)	84.4(5)
O(1)–Cr(1)–O(3)	96.8(5)	O(11)–Cr(2)–O(31)	95.4(4)
N(A1)–Cr(1)–O(3)	84.6(6)	N(B1)–Cr(2)–O(31)	85.(6)
O(1)–Cr(1)–O(2)	94.5(4)	O(11)–Cr(2)–O(21)	94.5(4)
O(2)–Cr(1)–O(3)	89.8(6)	O(21)–Cr(2)–O(31)	89.3(5)
Cr(1)–O(1)–Cr(1)′	120.0	Cr(2)–O(11)–Cr(2)′	120.0

$$3CrX_3\cdot(H_2O)_z + 6HO_2CR + 3L \longrightarrow [Cr_3O(O_2CR)_6(L)_3]X + 8HX + (z-1)H_2O \quad (1)$$

Thus, the need to use freshly prepared chromium(III) hydroxide or use an air-sensitive precursor is eliminated. The reaction protocol can be extended to carboxylic acids other than benzoic acid and its derivatives, such as to acetic acid (J. Vincent, unpublished results).

As almost all prior syntheses of these $Cr(III)_3$ species have been performed in water, benzoate complexes are quite rare and limited to two previous examples. The EPR spectrum of the first, presumably $[Cr_3O(o\text{-}O_2CC_6H_4Cl)_6(H_2O)_3][o\text{-}O_2CC_6H_4Cl]\cdot(H_2O)_x$, was reported in 1971; however, the specific composition and synthesis of the material was not provided [27]. The second, compound **4** [28, 29], was synthesized by the reaction of $Cr(NO_3)_3\cdot 9H_2O$ and benzoic anhydride and recrystallized from MeOH. Elemental analytical data and the solid state susceptibility at nine temperatures were reported; however, no mention of the yield or of any spectroscopic properties was made. The use of moisture-sensitive benzoic anhydride in the synthesis of **4** is avoided using the one-pot procedure.

Consequently, complexes **1–3** represent the first Cr(III) benzoate trimers with terminal ligands other than water; this has allowed X-ray structure quality crystals to be accessible. No structure of a Cr(III) trimer with terminal ligands other than water had been reported previously.

The synthesis of the unsymmetric $Cr(III)_3$ species, complex **6**, simply results from thermal stress.

Description of structure

Complex **1** crystallizes in the hexagonal space group $P\bar{6}$. Two independent Cr_3 cations are arranged such that the C_3 axis is perpendicular to both Cr_3 planes and passes through the central oxygens O(1) and O(11). An ORTEP projection of cation 1 is shown in Fig. 1.

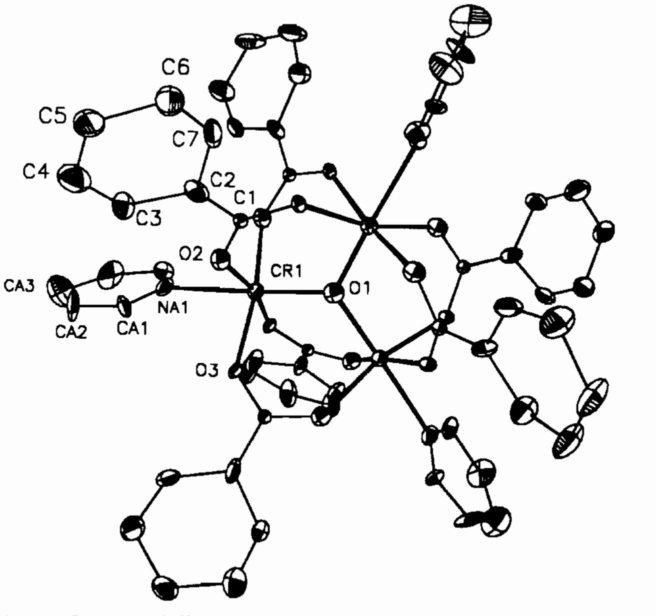

Fig 1. Structural diagram of cation 1 of $[Cr_3O(O_2CPh)_6(py)_3]ClO_4$ (**1**). Thermal ellipsoids are at 50% probability.

Each cation possesses imposed C_{3h} symmetry such that each set of three chromic ions is an equilateral triangle. Thus, Cr(1), O(1) and N(A1) are coplanar; likewise, Cr(2), O(11) and N(B1) are coplanar. The coordination about the chromic centers is slightly distorted octahedral with four oxygen atoms from bridging benzoate groups, the central triply-bridging oxygen, and a terminal pyridine nitrogen atom completing coordination to each trivalent ion. Each cation, thus, possesses the 'basic carboxylate' type structure found for many transition metal complexes [2]. This is the first example of a structurally characterized basic carboxylate complex of all chromic ions with terminal ligands other than water [1, 30–36]. All Cr–O bond lengths fall within the ranges of the previously characterized complexes. The structure of the cations is also similar to the mixed valent $Cr(III)_2Cr(II)$ complexes $Cr_3O(O_2CCF_2H)_6(py)_3$ and $Cr_3O(O_2CCF_2H)_6(4\text{-CNpy})_3$ [37]. However, in these complexes, the pyridine rings are coplanar with the Cr_3 units. In complex **1**, the pyridine rings are essentially perpendicular to the Cr_3O planes, probably as a result of increased steric interactions between the pyridine rings and the phenyl rings of the benzoate ligands [10].

Also of interest is the difference in the Cr–O(oxide) and Cr–N distances of the cations of complex **1**: Cr(1)–O(1), 1.883, Cr(1)–N(A1), 2.25; Cr(2)–O(11), 1.903, Cr(2)–N(B1), 2.04 Å. The short Cr–O bond is *trans* to the long Cr–N bond and vice versa.

The anion of complex **1** is unexceptional.

Electronic spectroscopy

The visible spectra of pseudo-octahedral chromium(III) complexes are expected to display two dominant bands, corresponding to the spin-allowed ${}^4A_{2g}\rightarrow{}^4T_{2g}$ and ${}^4A_{2g}\rightarrow{}^4T_{1g}(F)$ transitions. The trinuclear benzoate complexes, like their acetate counterparts, are not exceptions with these bands at *c.* 580–590 and 430–440 nm, respectively (Fig. 2 and Table 4). A series of weaker transitions at lower energy corresponding to formally spin-forbidden transitions result in weak bands between *c.* 660 and 730 nm. A third spin-allowed d–d transition is expected in the UV region but cannot be resolved from the ligand $\pi\rightarrow\pi^*$ transitions.

Most interesting are two features which appear as shoulders at 348–352 and 358–362 nm. Previously, such features have been assigned to simultaneous pair excitations, where a d → d excitation occurs simultaneously at two chromiums [38, 39]. The results compiled in Table 4 are in agreement with this assignment; the two bands for the various species assigned to the spin-allowed transitions shift as the energies of the d → d transitions of the species shift.

Comparison of the spectra of the benzoate complexes of Table 4 with those of the acetate complexes reveals that the nature of the R group of the carboxylate has little effect on the electronic spectra of these trinuclear

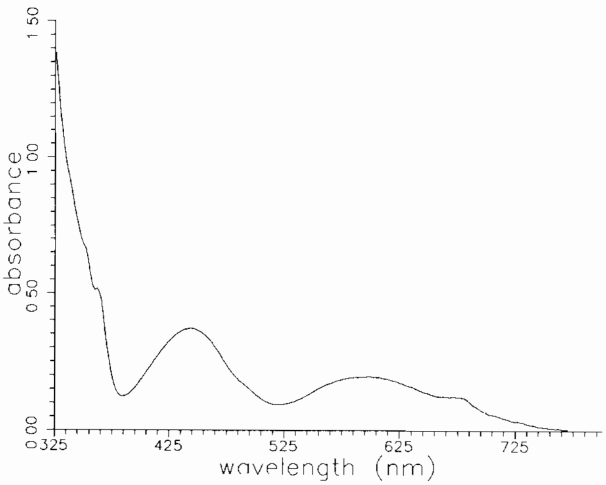

Fig. 2. Electronic spectrum of MeCN solution of complex **6** (6.03 mM Cr)

complexes, as has been suggested previously [40]. The nature of the terminal ligand, however, does appreciably effect the ligand field of the chromium ions; complexes with pyridine as the terminal ligand have larger ligand field splitting than complexes with terminal aqua ligands. The changes in splitting are essentially identical whether R is Me or Ph.

Note for complex **6** the energy of the d → d transitions is intermediate between those of the complexes where the terminal ligands are all pyridine or all water (Table 4); this is consistent with the $(py)_2(OH)$ formulation. The presence of the two features at 352 and 362 nm in the spectrum of **6** (Fig. 2) indicates **6** retains a multinuclear configuration.

Infrared spectroscopy

For a series of trinuclear Cr(III) acetate and formate complexes and their deuterio analogues, Cannon and co-workers [19, 39] have convincingly assigned the IR spectra and identified the vibrational modes of the central Cr_3O modes. Assuming D_{3h} symmetry for the core of the symmetric complexes, the planar Cr_3O unit should have four fundamental vibrational modes. The highest in energy of these is doubly degenerate, E′; and for Cr_3O complexes, this band was assigned to a strong transition at 640–660 cm^{-1} [19]. When one of the Cr(III) ions is replaced with Fe(III), the degeneracy is removed; and the band splits [39].

As shown in Table 5, a similar approach has been taken to assign the spectra of the trinuclear benzoate complexes. For all the symmetric complexes, a strong band at *c.* 640 cm^{-1}, which does not shift in the deuterio analogues, has been assigned to the E′ vibration of the Cr_3O unit. For the unsymmetric species **6**, where one of the pyridine ligands is replaced, the D_{3h} symmetry no longer exists. While the loss of pyridine is readily evident from loss of intensity of pyridine-derived features in the spectrum of the unsymmetric species versus the symmetric complexes with three pyridine ligands, the *c.* 640 cm^{-1} feature is retained. Thus, loss of symmetry in the terminal ligands is insufficient to result in breakdown of the effective symmetry about the Cr_3O core; but this provides conclusive evidence for retention of the Cr_3O core structure.

For the aqua complexes, substituting the H_2O with D_2O resulted in no clearly discernable changes in the lower energy portion of the IR spectra; consequently, locating the transitions corresponding to vibrations of the coordinated water was not possible.

NMR spectroscopy

A recent study [18] has shown that the ^1H NMR spectra of oxo-centered trinuclear chromium carboxylate assemblies possess readily discernable signals, despite the long electronic spin-lattice relaxation time of the chromic ions; this results from the reduction of the effective magnetic moment per Cr as the chromium centers are antiferromagnetically coupled. As shown in Table 6, complexes **1–6** all possess paramagnetically-shifted resonances in their ^1H NMR spectra, although signals resulting from protons in closest proximity to the metal centers are broadened beyond detection. However, in combination with ^2H NMR, all proton/deuteron signals can be observed [18].

TABLE 4. UV–Vis spectra of trinuclear chromium compounds

Compound	λ_{max} (nm) (ϵ/Cr) (M^{-1} cm^{-1})	Reference
$[Cr_3O(O_2CPh)_6(py)_3]ClO_4$[a]	352(124), 362(99.1), 434(79.0), 568(47.1), 682(15.8), ~710(sh), ~730(sh)	this work
$[Cr_3O(O_2CPh)_6(py)_3]Cl$[a]	352(136), 362(107), 434(87.2), 570(51.0), 682(14.6), ~710(sh), ~730(sh)	this work
$[Cr_3O(p\text{-toluate})_6(py)_3]ClO_4$[a]	352(137), 362(116), 432(80.5), 564(48.4), 682(19.1), ~710(sh), ~730(sh)	this work
$[Cr_3O(O_2CPh)_6(py)_2(OH)]$[a]	352(110), 362(857), 444(61.4), 664(20.7), ~710(sh)	this work
$[Cr_3O(O_2CPh)_6(H_2O)_3]NO_3$[b]	348(79.8), 358(59.3), 442(57.8), 590(49.7), ~660(sh), ~720(sh)	this work
$[Cr_3O(O_2CPh)_6(H_2O)_3]ClO_4$[c]	348(79.3), 358(59.2), 434(52.2), 592(45.8), ~660(sh), ~720(sh)	this work
$[Cr_3O(O_2CMe)_6(py)_3]^+$[d]	351, 361, 435, 565, 678, 703, 724	38
$[Cr_3O(O_2CMe)_6(H_2O)_3]^+$[d]	332, 339, 358, 442, 585, 656(sh), 671(sh), 702(sh), 717	38

[a]DMF. [b]MeCN. [c]$(CH_3)_2CO$. [d]Diffuse reflectance spectra.

TABLE 5. IR spectra (cm^{-1}) of selected complexes

$[Cr_3O(O_2CPh)_6(NC_5D_5)_3]ClO_4$	$[Cr_3O(O_2CC_6D_5)_6(py)_3]ClO_4$	1	2	Assignment
1630(br, vs)	1620(br, vs)	1620(br, vs)	1615(br, vs)	O_2CPh/py
1590(vs)	1580(s)	1570(vs)	1580(vs)	O_2CPh
	1560(s)			$O_2CC_6D_5$
1510(s)				C_5D_5N
1330(s)	1310(m)	1310(w)	1330(w)	O_2CPh
	1230(m)	1225(m)	1225(m)	py
1190(m)		1185(m)	1185(m)	O_2CPh
	1180(w)			$O_2CC_6D_5$
1175(m)		1170(m)	1170(m)	O_2CPh
	1170(w)			$O_2CC_6D_5$
1160(w)		1155(m)		O_2CPh
1090(br, vs)	1090(br, vs)	1100(br, vs)		ClO_4
	1050(m)	1050(w)		py
1030(m)	1040(w)			
	1020(m)	1030(m)	1020(m)	py
1010(w)				
985(m)				NC_5D_5
	965(m)			$O_2CC_6D_5$
940(w)		940(w)	940(m)	O_2CPh
895(m)				NC_5D_5
	880(s)			$O_2CC_6D_5$
	850(s)			$O_2CC_6D_5$
840(m)		850(m)	850(m)	O_2CPh
820(w)		820(w)	820(w)	O_2CPh
	815(s)			
	755(s)	755(s)	755(s)	py
	735(s)			
720(vs)		720(vs)	720(vs)	O_2CPh
	700(vs)	700(vs)	700(s)	py
685(s)		690(vs)	680(s)	O_2CPh
	640(vs)	650(vs)	640(vs)	Cr_3O
	620(vs)	610(m)	610(sh)	py
615(s)				NC_5D_5
600(sh)				NC_5D_5
	545(w)			$O_2CC_6D_5$
540(s)				NC_5D_6
520(vs)	515(vs)	520(vs)	515(vs)	$O_2CPh/O_2CC_6D_5$
	440(m)			$O_2CC_6D_5$

TABLE 6. ^{1}H NMR[a] of trinuclear chromium compounds in d_3-MeCN

Compound	Chemical shift (ppm)	Reference
$[Cr_3O(O_2CPh)_6(py)_3]ClO_4$	py: 2H, n.o.,[b] 3H, +11.2; 4H, −14.4 O_2CPh σ, n.o.;[d] m, +7.4; p, +0.5	18
$[Cr_3O(O_2CPh)_6(py)_3]Cl$	py: 2H, n.o.; 3H, +11.3; 4H, −14.4 O_2CPh: σ, n.o.; m, +7.4; p, +0.5	this work
$[Cr_3O(O_2CPh)_6(H_2O)_3]NO_3$	O_2CPh: σ, n.o.; m, +7.4; p, +0.5	this work
$[Cr_3O(O_2CPh)_6(H_2O)_3]ClO_4$	O_2CPh: σ, n.o; m, +7.4; p, +0.6	this work
$[Cr_3O$(*p*-toluate)$_6(py)_3]ClO_4$	py: 2H, n.o.; 3H, +11.2[c]; 4H, −14.4 *p*-tol: σ, n.o.; m, +7.4; CH_3, +11.2[c]	18
$[Cr_3O(O_2CPh)_6(py)_2(OH)]$	py: 2H, n.o.; 3H, +11.3[e]; 4H, −13.1 O_2CPh: σ, n.o.; m, +7.4; p, +0.5	this work

[a] n.o. = not observed. [b] ^{2}H NMR, −44.8 ppm. [c] Integration fits for two overlapping signals. [d] ^{2}H NMR, +3.2 ppm. [e] Intensity ratio 3H: m = 1.0:3.1.

The ^{1}H NMR spectrum of **1** displays four distinct resonances. Two of these resonances ($+11.2$ and -14.4 ppm) can be readily assigned to the pyridine ligand as they disappear in the ^{1}H NMR of the NC_5D_5 derivative. The third pyridine resonance is readily located for the NC_5D_5 derivative by ^{2}H NMR. (By using ^{2}H NMR, signals in a given environment should be narrower than the corresponding ^{1}H NMR signal by up to $\gamma_H{}^2/\gamma_D{}^2 = 42.5$, where γ_H and γ_D are the gyromagnetic ratios of the proton and deuteron, respectively.) The broadness ($H4 < H3 \ll H2$) of these signals readily allows them to be assigned. The alternating sense of shift between the 3-position and 4-position protons (downfield and upfield) is consistent with a π delocalization mechanism, that expected for a $t_{2g}{}^3$ ion. (Also dipolar contributions to the isotropic shifts should be minimal for a $t_{2g}{}^3$ ion.)

The other two resonances in the ^{1}H NMR spectrum of **1** can readily be assigned to the benzoate ligand, with the *ortho* proton broadened beyond detection. The *ortho*-deuteron is readily located in the ^{2}D NMR of the deutero-benzoate analogue (Fig. 3). The ^{1}H resonance at $+0.5$ ppm disappears in the *p*-toluate derivative, **3**, and is replaced by a new resonance at $+11.2$ ppm. Hence, the $+0.5$ ppm signal and the $+7.4$ ppm signals are readily assigned to the *para* and *meta* protons, respectively. Note the *para*-methyl proton resonance of the toluate ligand is shifted downfield, in contrast to the *para*-proton resonance which is shifted upfield compared to free benzoate, providing conclusive evidence for the existence of a dominant π delocalization pathway.

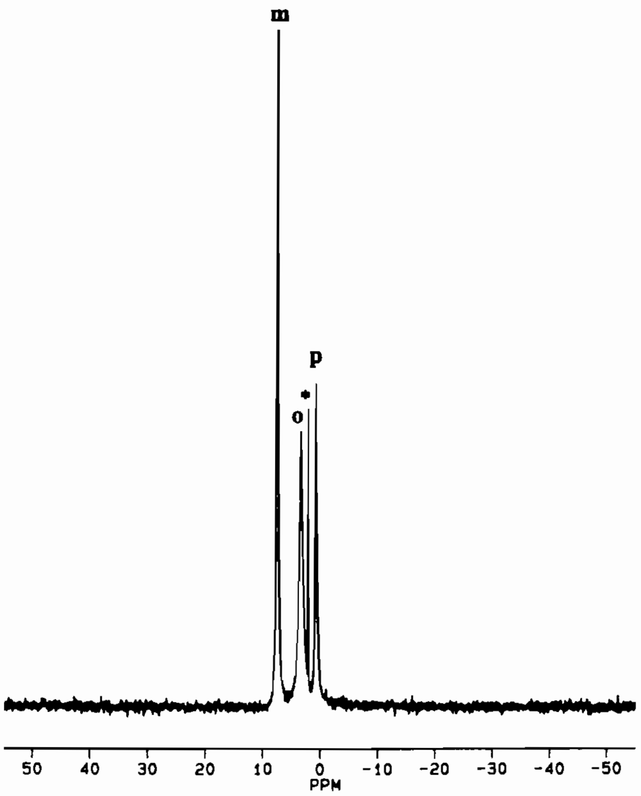

Fig. 3. ^{2}H NMR spectrum of $[Cr_3O(O_2CC_6D_5)_6(py)_3]ClO_4$ in MeCN. * = solvent.

The resonances of the pyridine and benzoate ligands of the other trinuclear complexes are essentially identical to those of these ligands in complexes **1** and **3** (Table 6). This provides evidence that the unsymmetric complex **6** possesses approximately the same structure and coupling as the symmetric complexes. Integration of the ^{1}H NMR resonances of **6** produces a pyridine to benzoate ratio of 2:3.1, within error of the expected 2:3 ratio.

Mass spectrometry

FAB mass spectra of these trinuclear complexes as DMF or DMF/glycerol solutions all display a distinctive set of ions with masses corresponding to the series $[Cr_3O(O_2CR)_x]^+$, $x = 4$, 5 or 6, regardless of the nature of the carboxylate (Table 7). In some cases the ion corresponding to $x = 3$ is observable. For the aqua-containing trimers, the aqua ligands are lost, such that the parent ion is not observed. When the terminal ligands are pyridine, the parent ion is observable in some cases along with ions derived from successive loss of pyridine molecules (Table 7). Similar terminal ligand loss has recently been observed in electrospray mass spectrometric studies of trinuclear Cr(III) assemblies [41]. Loss of carboxylates was only observed in collisionally activated decomposition mass spectrometric studies [41].

For the unsymmetric complex **6**, the observed ions are exactly those expected if the hydroxo (aqua) ligand is lost as in the symmetric aquo complexes (Table 7). This provides strong evidence for the proposed formulation and structure of **6**; however, ions resulting from rearrangement reactions in the spectrometer have been observed for larger Cr carboxylate assemblies (J. Vincent, unpublished results).

Magnetic susceptibility studies

The chromic ions ($S = 3/2$) of trinuclear oxo-centered chromium(III) carboxylate assemblies are antiferromagnetically coupled with a coupling constant (J) of *c.* -10 cm^{-1} ($H = -2JS_1 \cdot S_2$), resulting in an $S = 1/2$ ground state [2]. Consequently, the room temperature magnetic moments of these complexes ($T = 290$–298 K) are generally in the range 3.1–3.5 BM. The solid and solution room temperature magnetic moments of complexes **1**–**6** (including the unsymmetric complex) fall within this range (Table 8).

ESR spectroscopy

At low temperatures where only the $S = 1/2$ ground state of the coupled trinuclear assemblies is substantially populated, the ESR spectra of these complexes are

TABLE 7. Mass spectra of trinuclear chromium complexes

Compound	Mass	Assignment	Relative height (%)
$[Cr_3O(O_2CPh)_6(H_2O)_3]NO_3$	898	$[Cr_3O(O_2CPh)_6]^+$	100
	777	$[Cr_3O(O_2CPh)_5]^+$	97
	656	$[Cr_3O(O_2CPh)_4]^+$	80
	535	$[Cr_3O(O_2CPh)_3]^+$	86
$[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$	526	$[Cr_3O(O_2CMe)_6]^+$	100
	467	$[Cr_3O(O_2CMe)_5]^+$	36
	408	$[Cr_3O(O_2CMe)_4]^+$	21
$[Cr_3O(O_2CPh)_6(py)_3]ClO_4$	1135	$[Cr_3O(O_2CPh)_6(py)_3]^+$	13
	1056	$[Cr_3O(O_2CPh)_6(py)_2]$	36
	997	$[Cr_3O(O_2CPh)_6(py)]^+$	45
	898	$[Cr_3O(O_2CPh)_6]^+$	100
	856	$[Cr_3O(O_2CPh)_5(py)]^+$	6
	777	$[Cr_3O(O_2CPh)_5]^+$	51
	656	$[Cr_3O(O_2CPh)_4]^+$	28
	535	$[Cr_3O(O_2CPh)_3]^+$	30
$[Cr_3O(O_2CPh)_6(py)_2(OH)]$	1056	$[Cr_3O(O_2CPh)_6(py)_2]^+$	25
	977	$[Cr_3O(O_2CPh)_6(py)]^+$	43
	898	$[Cr_3O(O_2CPh)_6]^+$	100
	777	$[Cr_3O(O_2CPh)_5]^+$	48
	656	$[Cr_3O(O_2CPh)_4]^+$	25
	535	$[Cr_3O(O_2CPh)_3]^+$	25
$[Cr_3O(p\text{-toluate})_6(py)_3]ClO_4$	1140	$[Cr_3O(p\text{-toluate})_6(py)_2]^+$	8
	1061	$[Cr_3O(p\text{-toluate})_6(py)]^+$	21
	982	$[Cr_3O(p\text{-toluate})_6]^+$	100
	847	$[Cr_3O(p\text{-toluate})_5]^+$	34
	712	$[Cr_3O(p\text{-toluate})_4]^+$	18
	577	$[Cr_3O(p\text{-toluate})_4]^+$	21

TABLE 8. Magnetic moments of trinuclear chromium complexes

	μ/Cr (solid state) (BM)	μ/Cr (Evans) (BM)
$[Cr_3O(O_2CPh)_6(py)_3]ClO_4$	3.10	[a]
$[Cr_3O(O_2CPh)_6(py)_3]Cl$	3.10	3.19[b]
$[Cr_3O(O_2CPh)_6(H_2O)_3]NO_3$	3.05	3.31[c]
$[Cr_3O(O_2CPh)_6(H_2O)]ClO_4$	3.15	3.06[d]
$[Cr_3O(O_2CPh)_6(py)_2(OH)]$	3.39	[a]
$[Cr_3O(p\text{-toluate})_6(py)_3]ClO_4$	3.17	3.18[d]

[a]Insufficient solubility. [b]d-chloroform. [c]d_6-DMSO. [d]d_3-MeCN.

comprised of a single signal with a *g* value of ~2 (for example, see refs. 27, 40, 42). The spectra of the trinuclear benzoate species are no exception. For example as shown in Fig. 4(b), the ESR spectrum of an ethanol glass of complex **4** at 10.8 K reveals a sharp signal at an apparent *g* value of ~2.0, nearly identical to that reported for polycrystalline $[Cr_3O(O_2CMe)_6(H_2O)_3]^+$ at 4.2 K [40]. In contrast, the powder spectrum of unsymmetric complex **6** displays a signal with somewhat more asymmetry (*g* apparent = 2.0) (Fig. 4(a)). Such asymmetry, however, is not atypical and has previously been observed for polycrystalline samples of trinuclear acetate complexes at low temperature [42]. This spectrum suggests that **6** is not a mixture of symmetric $(py)_3$ or symmetric $(H_2O)_3$ complexes but a unique species.

Supplementary material

Additional material comprising all bond distances and angles, thermal parameters, and structure factor amplitudes are available from author J.B.V. on request.

Acknowledgements

Acknowledgement is made to the Research Grants Committee of the University of Alabama (J.B.V.), to the Research Experiences for Minority Undergraduate Students Program of the National Science Foundation (M.M.G.), and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society (J.B.V.), for support of this research.

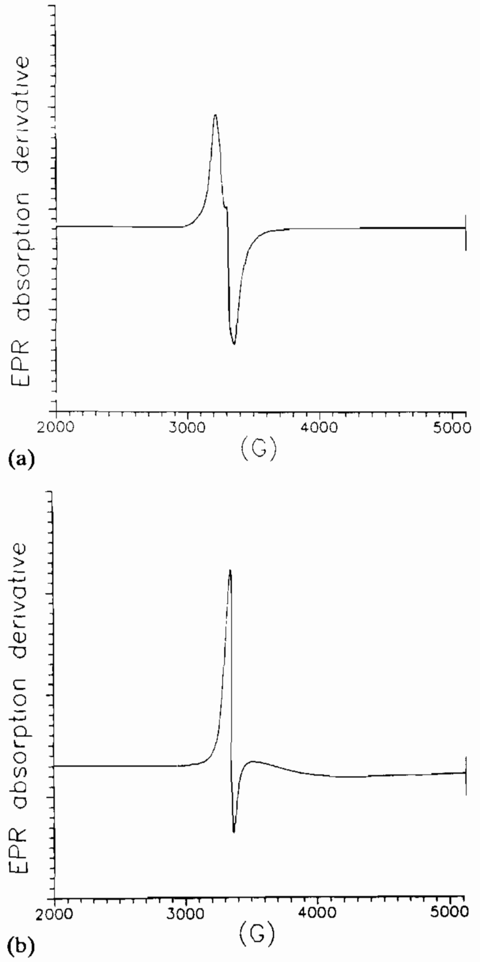

Fig. 4. (a) Powder EPR spectrum of complex **6**. (b) EtOH glass EPR spectrum of complex **4**. Conditions: 10.8 K; gain, (a) 2×10^2, (b) 8; scan time, 4 min; time constant, 0.25 s; modulation amplitude, 10 G; fieldset, 2600 G; scan range, 5000 G; power, 1 mW; frequency, 9.2 GHz.

References

1 B.N. Figgis and G.B. Robertson, *Nature (London), 205* (1965) 694.

2 R.D. Cannon and R.P. White, *Prog Inorg Chem, 36* (1988) 195.

3 A. Earnshaw, B.N. Figgis and J. Lewis, *J Chem Soc. A,* (1966) 1656.

4 L. Dubicki and P. Day, *Inorg. Chem., 11* (1972) 1868.

5 B.S. Tsukerblat, M.I. Belinskii and B.Y. Kuyavskaya, *Inorg Chem., 22* (1983) 995.

6 J.B. Vincent, H.-R. Chang, K. Folting, J.C. Huffman, G. Christou and D.N. Hendrickson, *J. Am. Chem. Soc., 109* (1987) 5703.

7 S.M. Oh, D.N. Hendrickson, K.L. Hassett and R.E. Davis, *J. Am. Chem. Soc., 106* (1984) 7984.

8 S.M. Oh, D.N. Hendrickson, K.L. Hassett and R.E. Davis, *J Am. Chem Soc, 107* (1985) 8009.

9 G. Christou, *Acc. Chem. Res, 22* (1989) 328.

10 J.B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P.D.W. Boyd, J.C. Huffman, D.N Hendrickson and G. Christou, *J. Am Chem Soc., 111* (1989) 2086.

11 D.W. Low, D.M. Eichhorn, A. Draganesco and W.H. Armstrong, *Inorg Chem., 30* (1991) 878.

12 D F. Harvey, C.A. Christmas, J.K. McCusker, P.M. Hagen, R.K. Chadha and D.N. Hendrickson, *Angew Chem, Int. Ed. Engl., 30* (1991) 598.

13 A. Bino, R. Chayat, E. Pedersen and A. Schneider, *Inorg. Chem., 30* (1991) 856.

14 A.S. Batsanov, G A. Timko, Y.T. Struchkov, N.V. Gerbeleu and K.M. Indrichan, *Koord Khim., 17* (1991) 662.

15 R. Weinland and J. Lindner, *Z. Anorg. Chem., 190* (1930) 285.

16 R.F. Weinland and H. Hachenburg, *Z. Anorg Chem., 126* (1923) 285.

17 A Werner, *Ber Dtsch Chem. Ges, 41* (1908) 3447.

18 M.M. Glass, K. Belmore and J. Vincent, *Polyhedron, 12* (1993) 133.

19 M.K. Johnson, D.B. Powell and R.D. Cannon, *Spectrochim. Acta, Part A, 37* (1987) 995.

20 D.F. Evans, *J. Chem. Soc.,* (1959) 2003.

21 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Dalton Trans.,* (1979) 45.

22 G.M. Sheldrick, SHELX 76, a system of computer programs for X-ray structure determination, University of Cambridge, UK, 1976.

23 G.M. Sheldrick, in G.M. Sheldrick, C. Kruger and R. Goddard (eds.), *Crystallographic Computing 3,* Oxford University Press, London, 1986, pp. 175–189.

24 A. Earnshaw, B.N. Figgis and J. Lewis, *J. Chem Soc. A,* (1966) 1656.

25 S. Uemara, A. Spencer and G. Wilkinson, *J. Chem Soc, Dalton Trans.,* (1973) 2565.

26 T. Szymanska-Buzar and J.J. Ziolkowski, *Sov J. Coord. Chem., 2* (1976) 897.

27 Y. V. Yablokov, V.A. Gaponenko and V.V. Zelentsov, *Sov. Phys. Solid State, 13* (1971) 1081.

28 V.V. Zelentsov, T.A. Zhemchuzhnikova, Y.V. Yablokov and K.M. Yakubov, *Dokl. Akad Nauk SSSR, 216* (1974) 844.

29 V.V. Zelentsov, T.A. Zhemchuznikova, Y.V. Rakitin, Y.V. Yablokov and K.M. Yakubov, *Koord. Khim., 1* (1975) 194.

30 S.C. Chang and G.A. Jeffrey, *Acta Crystallogr., Sect B., 26* (1970) 673.

31 T. Glowiak, M. Kubiak and B. Jezowska-Trebiatowska, *Bull Acad. Pol. Sci, 25* (1977) 359.

32 E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, M. Sabat and J.A. Ibers, *Inorg Chim. Acta, 66* (1982) 115.

33 A.S. Antsyshkina, M.A. Porai-Koshits, I.V. Arkhangel'skii and I.N. Diallo, *Russ. J. Inorg. Chem., 32* (1987) 1700.

34 J.E. Bradshaw, D.A. Grossie, D.F. Mullica and D.E. Pennington, *Inorg Chim. Acta, 141* (1988) 41.

35 H Kato, K. Nakata, A. Nagasawa, T. Yamaguchi, Y. Sasaki and T. Ito, *Bull. Chem Soc. Jpn., 64* (1991) 3463.

36 D.F. Mullica, D.E. Pennington, J.E. Bradshaw and E.L. Sappenfield, *Inorg Chim. Acta, 191* (1992) 3.

37 F.A. Cotton and W. Wang, *Inorg. Chem., 21* (1982) 2675.

38 A. B. Blake, A. Yavari, W.E. Hatfield and C.N. Sethulekshmi, *J Chem. Soc., Dalton Trans.,* (1985) 2509.

39 M.K. Johnson, R.D. Cannon and D.B. Powell, *Spectrochim Acta, Part A, 38* (1982) 307.

40 V.A. Gaponenko, M.V. Eremin and Y.V. Yablokov, *Sov Phys. Solid State, 15* (1973) 909.

41 A. van den Bergen, R. Colton, M. Percy and B.O. West, *Inorg Chem, 32* (1993) 3408.

42 Y.V. Yablokov, V.A. Gaponenko, A.V. Ablov and T.N. Zhikhareva, *Sov. Phys Solid State, 15* (1973) 251.