# Correlations between Nuclear Magnetic Resonance Spectra and Crystal Structures. A Carbon-13 Nuclear Magnetic Resonance Study in the Solid State of the Group 15 Xanthates $[A(S_2COR)_3]$ (A = $As^{III}$, $Sb^{III}$, or $Bi^{III}$; R = Me, Et, or $Pr^i$)

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The $^{13}C$ cross-polarisation magic angle spinning (c.p.m.a.s.) n.m.r. spectra of solid $[A(S_2COR)_3]$ (A = $As^{III}$ or $Sb^{III}$; R = Me, Et, or $Pr^i$; A = $Bi^{III}$; R = Me or $Pr^i$) exhibit systematic features which correlate well with the known crystal structures. In the case of $[Bi(S_2COEt)_3]$, for which no crystal structure is available, the $^{13}C$ c.p.m.a.s. n.m.r. spectrum is consistent with this species crystallising as two polymorphs, and their gross structural features are deduced through the correlations of spectra with structures drawn from the preceding eight Group 15 xanthates. The species $K(S_2COMe)$ and $K(S_2COPr^i)$ have been studied similarly.

Solid-state $^{13}C$ c.p.m.a.s. n.m.r. spectroscopy, incorporating cross polarisation (c.p.), magic angle spinning (m.a.s.), and high power proton decoupling, often provides high-resolution spectra from which considerable structural information may be deduced.[1,2] In contrast to the solution state where conformational changes and similar intramolecular processes tend to occur rapidly, molecular conformations tend to be 'locked' in the solid state. Thus a molecular moiety which is characterised by a single resonance in solution may give rise to several resonances in the solid state as a consequence of either the lowering of molecular symmetry due to conformational 'locking' or from purely crystallographic (intermolecular) effects. The opportunity then arises for drawing correlations between the $^{13}C$ c.p.m.a.s. n.m.r. spectra and the crystal structures of a series of related compounds, which may result in the elucidation of solid-state structures for crystallographically intractable species such as amorphous solids.

This approach is applied here to the Group 15 xanthates $[A(S_2COR)_3]$ where A = $As^{III}$, $Sb^{III}$, or $Bi^{III}$ and R = Me, Et, or $Pr^i$. Interest in this system stems from a wider investigation of the different modes of co-ordination adopted by xanthate ligands.[3–11] Crystallographic studies on the $[A(S_2COR)_3]$ series have revealed three different types of $AS_6$ co-ordination polyhedra at the core of the $[A(S_2COR)_3]$ molecule, and that the bidentate xanthate ligands co-ordinate asymmetrically with different A–S bond distances. No crystals of $[Bi(S_2COEt)_3]$ suitable for *X*-ray diffraction studies have so far been obtained. The aim of this study is to seek a correlation between the $^{13}C$ c.p.m.a.s. n.m.r. spectra and the crystal structures of $[A(S_2COR)_3]$, and on the basis of this correlation to assign a structure to $[Bi(S_2COEt)_3]$. The stoicheiometrically simpler $K(S_2COMe)$ and $K(S_2COPr^i)$ species, which in the solid state are characterised by non-equivalent xanthate anions in the unit cell,[7,8] are also examined for the reflection of these variations in their $^{13}C$ c.p.m.a.s. n.m.r. spectra.

## Experimental

*Materials.*—The potassium xanthates were precipitated from solution by addition of $CS_2$ to solutions of KOH in the appropriate alcohol. The Group 15 xanthates $[A(S_2COR)_3]$ where A = $As^{III}$,[3] $Sb^{III}$,[4] or $Bi^{III}$,[5] and R = Me, Et, or $Pr^i$, were prepared by literature methods. All were recrystallised from dichloromethane.

*N.M.R. Measurements.*—Carbon-13 c.p.m.a.s. n.m.r. spectra were run on a Bruker CXP-300 n.m.r. spectrometer at 75.47 MHz, with single cross-polarisation contacts of typically 1—2 ms using a $^1H$ field of $1.4 \times 10^{-3}$ T, and with magic angle sample spinning at 2.2—2.5 kHz in boron nitride rotors of the Andrew–Beams type. Spectral parameters were: spectral width 25 kHz, acquisition time 50 ms, and recycle time 5 s. Typically 1 000—5 000 transients of 1 028—2 056 data points were collected prior to Fourier transformation. In some cases the TOSS pulse sequence[12] was used to eliminate spinning side bands where they made assignments difficult. All chemical shifts were referenced to an internal delrin [poly(oxymethylene), $(CH_2O)_n$] sample (δ 88.5 p.p.m.).

## Results and Discussion

The crystal structure of $K(S_2COMe)$ shows that there are three unique xanthate ligands in the crystallographic asymmetric unit as a consequence of three different potassium ion geometries.[7] These xanthate ligands fall into two classes: (*i*) with similar C–S bond distances of 1.679(2) and 1.686(2) Å [one ligand (a)], and (*ii*) with significantly different C–S bond distances of 1.667(2) and 1.693(2), and 1.670(2) and 1.700(2) Å [two ligands (b) and (c)].[7] The solid-state $^{13}C$ c.p.m.a.s. n.m.r. spectrum of $K(S_2COMe)$ contains two methyl resonances at 62.8 and 61.7 p.p.m. in the integrated area ratio 2:1 respectively, and two broadened $S_2CO$ resonances at 235.4 and 233.6 p.p.m. in the integrated area ratio 2:1 respectively. In principle, separate resonances are anticipated for the methyl and $S_2CO$ carbons for each of the xanthate ligands (a), (b), and (c), but in practice two resonances are observed in the area ratio 2:1 which indicates that two of the xanthate ligands experience magnetic equivalence. In solution the xanthate ligand inequivalences are removed and $^{13}C$ resonances are observed at 62.4 and 235.6 p.p.m.

The crystal structure of $K(S_2COPr^i)$ shows that two $S_2COPr^{i-}$ constitute the asymmetric unit[8] (as a consequence of there being two distinct potassium ion geometries) on which basis four methyl, two methine, and two $S_2CO$ resonances are expected in the $^{13}C$ c.p.m.a.s. n.m.r. spectrum. In practice two methyl resonances are observed at 23.0 and 22.2 p.p.m. (broad) in the area ratio 1:3, two methine resonances are observed at 78.6 and 77.0 p.p.m. in the area ratio 1:1, and a single resonance is observed for $S_2CO$ at 232.4 p.p.m. The resolution of the

**Table.** Carbon-13 c.p.m.a.s. n.m.r. spectroscopic data (p.p.m.)

| Compound | $CH_3$ | $CH_2$ | CH | $S_2CO$ | Structure type[a] | Solution values[b] |
|---|---|---|---|---|---|---|
| $K(S_2COMe)$ | 62.8, 61.7 | | | 235.4, 233.6 | | 62.4, 235.6[c] |
| $K(S_2COPr^i)$ | 23.0, 22.2 | | 78.6, 77.0 | 232.4 | | 23.9, 81.0, 235.1[c] |
| $[As(S_2COMe)_3]$ | 62.1 | | | 216.0 | A | 61.3, 217.7 |
| $[As(S_2COEt)_3]$ | 13.7 | 74.1 | | 216.5 | A | 13.9, 71.5, 216.9 |
| $[As(S_2COPr^i)_3]$ | 22.7, 21.9 | | 79.9 | 217.2 | A | 21.4, 80.0, 216.1 |
| $[Sb(S_2COMe)_3]$ | 65.1, 64.4, 62.4 | | | 224.0, 219.5 | B | 61.8, 223.3 |
| $[Sb(S_2COEt)_3]$ | 14.5 | 75.4 | | 222.1 | A | 13.9, 72.0, 222.4 |
| $[Sb(S_2COPr^i)_3]$ | 22.8, 21.7 | | 81.2 | 222.2 | A | 21.4, 80.7, 221.6 |
| $[Bi(S_2COMe)_3]$ | 64.7, 63.7, 62.4 | | | 225.7, 224.2 | B | 60.9, 226.8 |
| $[Bi(S_2COEt)_3]$ | 16.1, 15.1, 14.5, 13.8, 12.6 | 75.9, 71.3, 69.8 | | 228.8, 226.4 | ? | 13.9, 71.3, 225.8 |
| $[Bi(S_2COPr^i)_3]$ | 25.0, 23.3, 21.7 | | 83.7, 82.3 | 225.3, 224.3 | C | 21.5, 80.3, 224.9 |

[a] See Figure 1. [b] See ref. 6 for $[A(S_2COR)_3]$ compounds; measured in $CDCl_3$ solution. [c] In $D_2O$ solution.

methyl and $S_2CO$ resonances is less than desirable, but the overall spectrum is consistent with the crystallographic inequivalences.

*X*-Ray crystallographic studies show the Group 15 xanthates to exist as three different structure types, A, B, and C, as shown in Figure 1. The $[As(S_2COR)_3]$ compounds where R = Me (which crystallises as two polymorphs as discussed later),[9,10] Et,[3] or $Pr^i$,[5] and the $[Sb(S_2COR)_3]$ compounds where R = Et[4,11] or $Pr^i$,[5] are of type A (Figure 1). Type A structures are characterised by a crystallographic three-fold axis of symmetry passing through the central atom and in consequence all of the xanthate ligands are equivalent. The $^{13}C$ c.p.m.a.s. n.m.r. spectra of these compounds are consistent with these crystallographic observations. Single resonances are observed for each type of ligand carbon atom except in the case of $S_2COPr^i$ where two methyl resonances are observed as a consequence of the crystallographic inequivalence of the two methyl groups in each ligand (Table). In solution, single resonances are observed for each type of carbon in all cases. Crystallisation of $[As(S_2COMe)_3]$ from a variety of solvents produces two polymorphs.[9,10] One polymorph is isostructural (space group $R\bar{3}$) with the type A species in the Table, but in the second crystalline form (space group $P2_1/c$)[10] the two $[As(S_2COMe)_3]$ molecules comprising the asymmetric unit do not possess ideal three-fold symmetry. Thus the first polymorph should give rise to one resonance for each type of ligand carbon, and the second should produce six such resonances. In the $[As(S_2COMe)_3]$ polymorphic mixture (crystallised from dichloromethane) used in this study the $P2_1/c$ polymorph needles are more abundant than the $R\bar{3}$ polymorph blocks, but the observation of a single resonance for each type of ligand carbon for this mixture indicates that the crystallographic inequivalences of the $P2_1/c$ induce insufficient magnetic inequivalence for resolution of separate $^{13}C$ resonances.

The type B structures (Figure 1) are represented by the $[Sb(S_2COMe)_3]$ and $[Bi(S_2COMe)_3]$ compounds,[10] and have no crystallographically imposed symmetry such that each xanthate ligand is unique. They do, however, conform to a pseudo-mirror (*i.e.* non-crystallographic) symmetry which is convenient for further description of the structure. Thus in $[Bi(S_2COMe)_3]$ the xanthate ligand defining the approximate mirror plane forms Bi–S bonds of different lengths [2.596(3) and 2.998(4) Å], as do the ligands on either side of the mirror plane. However, for these two ligands in these cases the Bi–S bond distance differences are less as is seen from the values of 2.720(3) and 2.933(4) Å for one ligand and 2.747(3) and 2.961(4) Å for the other.[10] Similar variations are observed in the Sb–S

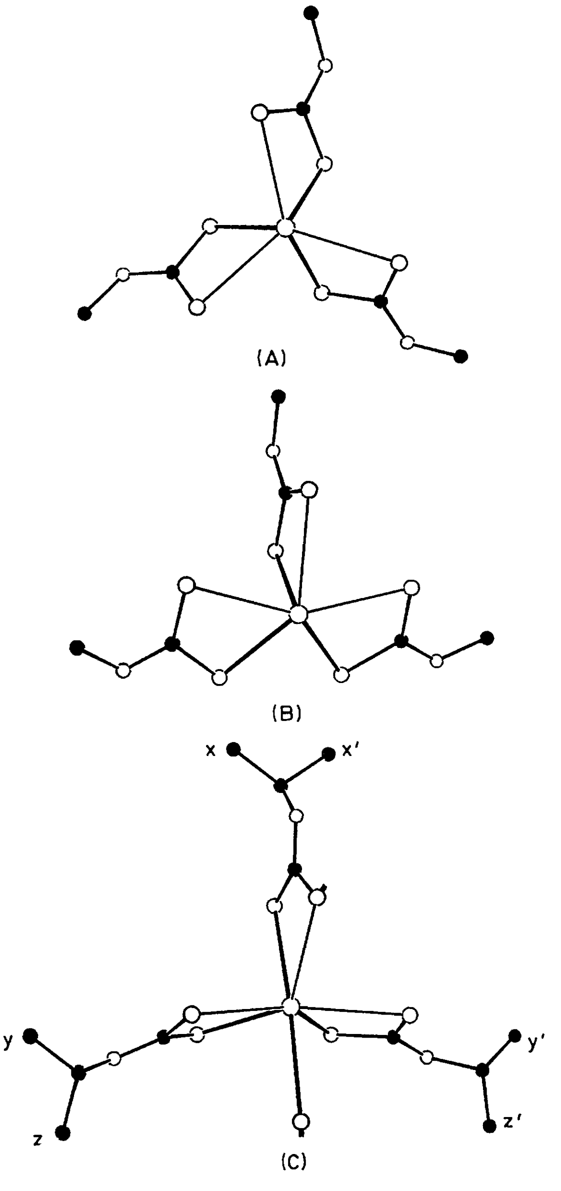

**Figure 1.** Different structure types found for Group 15 xanthates. Carbon atoms are filled and hydrogen atoms are omitted for clarity

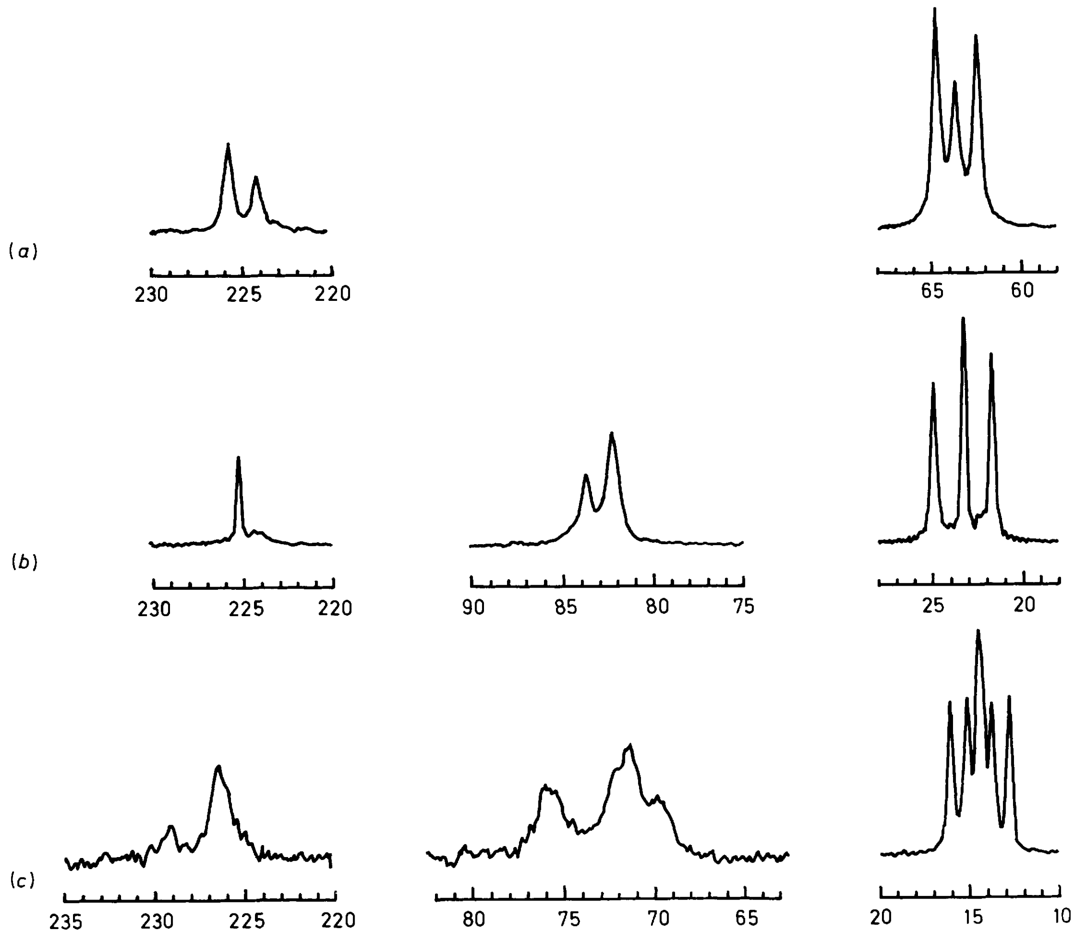

**Figure 2.** The $^{13}C$ c.p.m.a.s. n.m.r. spectra of (*a*) $[Bi(S_2COMe)_3]$, (*b*) $[Bi(S_2COPr^i)_3]$, and (*c*) $[Bi(S_2COEt)_3]$. The scale for each spectrum is in p.p.m., and the chemical shifts are relative to that of delrin (88.5 p.p.m.)

distances of $[Sb(S_2COMe)_3]$.[10] The three methyl resonances observed in the $^{13}C$ c.p.m.a.s. n.m.r. spectrum of $[Bi(S_2COMe)_3]$ [Figure 2(*a*)] are consistent with the inequivalence of the three xanthate ligands. Two resonances in the integrated area ratio *ca.* 2:1 are observed for $S_2CO$, and it is probable that the magnetic inequivalence of the two xanthate ligands on either side of the pseudo-mirror plane is insufficient for the resolution of their $S_2CO$ resonances. A similar spectrum is observed for $[Sb(S_2COMe)_3]$ as seen in the Table, from which it is also seen that the three xanthate ligands become equivalent in solution.

The sole example of a type C structure is $[Bi(S_2COPr^i)_3]$ in which bismuth(III) and the atoms of one xanthate ligand, except those of the methyl groups, lie on a crystallographic mirror plane and the two other xanthates are related to each other through this mirror plane.[5] One of the sulphur atoms on the mirror plane also co-ordinates a neighbouring bismuth(III), thereby generating a linear polymeric structure, with the consequence that each bismuth(III) is seven-co-ordinate. There are three pairs of equivalent methyl groups in the structure (labelled *x*, *y*, and *z* in Figure 1), two non-equivalent methine groups in the ratio 1:2 (xanthate ligand on mirror plane: xanthate ligands on either side of mirror plane), and similarly two non-equivalent $S_2CO$ in the ratio 1:2. The $^{13}C$ c.p.m.a.s. n.m.r. spectrum of $[Bi(S_2COPr^i)_3]$ [Figure 2(*b*)] exhibits three methyl resonances in the integrated area ratio 1:1:1, two methine resonances in the ratio 1:2, and two overlapping $S_2CO$ resonances where the broader of the two probably reflects the interaction of the xanthate ligand on the mirror plane with the second bismuth(III). Thus this spectrum is consistent with the symmetry relationships observed in the structure of $[Bi(S_2COPr^i)_3]$ determined by *X*-ray crystallography. In solution the three xanthate ligands become equivalent as indicated by their $^{13}C$ n.m.r. spectrum (Table).

The $[Bi(S_2COEt)_3]$ species, for which no crystal structure has been reported, provides an opportunity to attempt a structural assignment from its $^{13}C$ c.p.m.a.s. n.m.r. spectrum [Figure 2(*c*)]. The five methyl resonances are consistent with $[Bi(S_2COEt)_3]$ existing as two polymorphs containing the type B and type C structures, such that three resonances arise from the three unique methyls in the type B structure, and two, in the integrated area ratio 1:2 (xanthate ligand on the mirror plane: two equivalent xanthate ligands on either side of the mirror plane), arise from the type C structure. The relative areas of the methyl resonances suggest that the polymorphs are present in similar proportions. The methylene and $S_2CO$ multiplets are too broadened for definite structural conclusions to be drawn, but are generally consistent with the several magnetic environments anticipated for type B and C structures. It is reported that a preliminary *X*-ray study of a fragment of a $[Bi(S_2COEt)_3]$ crystal yielded unit-cell dimensions * suggesting that the crystal was isostructural with $[Bi(S_2COMe)_3]$ (type B,

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* Crystal data for $[Bi(S_2COEt)_3]$: triclinic, space group $P\bar{1}$, $a$ = 5.967(2), $b$ = 10.559(5), $c$ = 14.30(2) Å, $\alpha$ = 90.43(7), $\beta$ = 92.22(6), $\gamma$ = 100.58(3)°, and $U$ = 884.6 Å$^3$; *cf.* triclinic, space group $P\bar{1}$, $a$ = 5.924(3), $b$ = 10.499(3), $c$ = 12.485(4) Å, $\alpha$ = 95.99(3), $\beta$ = 101.76(4), $\gamma$ = 101.45(4)°, and $U$ = 736.6 Å$^3$ for $[Bi(S_2COMe)_3]$.[10]

Figure 1).[10] This lends support for the hypothesis, based on the $^{13}C$ c.p.m.a.s. n.m.r. spectrum, that our sample of $[Bi(S_2COEt)_3]$ was crystallised as two polymorphs rather than type B and C structures being incorporated into a single crystallographic unit cell. The $[Bi(S_2COEt)_3]$ sample was also crystallised from chloroform and benzene, and the resulting $^{13}C$ c.p.m.a.s. n.m.r. spectra closely resembled that of the sample crystallised from dichloromethane which is discussed above.

From the foregoing discussion, the $^{13}C$ c.p.m.a.s. n.m.r. spectra in Figure 2 and the data in the Table, it is seen that for the xanthate species studied the alkyl carbon atom resonances are better resolved than are those of $S_2\mathit{C}O$, and are accordingly more indicative of molecular and crystallographic inequivalence where it exists. In all cases such inequivalence is lost in solution, as indicated by the observation of single resonances for a given xanthate carbon in the solution spectrum, whereas more than one resonance is observed for that carbon in the solid-state spectrum (Table).

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