Solid-state High-resolution Carbon-13 Magnetic Resonance Spectra of Dithioacetate Complexes of Platinum, Palladium, and Nickel

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High-resolution ^{13}C n.m.r. spectra were measured for platinum, palladium, and nickel dithioacetato complexes with various structures and oxidation states in the solid state. The $[Pt_2(S_2CMe)_4]$ complex showed one methyl signal, while $[Ni_2(S_2CMe)_4]$ and $[Pd_2(S_2CMe)_4]$ showed two and three methyl signals, respectively. These results are well explained in terms of the single-crystal *X*-ray structures of these complexes. Compared with the spectrum of $[Pt_2(S_2CMe)_4]$, the quaternary carbon signal of $[Pt_2(S_2CMe)_4I_2]$ is shifted to lower-field, while the methyl signal appears at a similar position, indicating the greater effectiveness of Pt^{3+} over Pt^{2+} in removing electron density from the surrounding quaternary carbon atoms. The one-dimensional $[M_2(S_2CMe)_4I]$ (M = Ni or Pt) complexes showed two broad methyl signals owing to the slight magnetism.

To determine molecular structures in the solid state, *X*-ray crystal analyses are preferable. However, they are time consuming and are sometimes impossible if single-crystals are unobtainable. Recently, high-resolution solid-state ^{13}C cross polarization magic angle spinning (c.p.m.a.s.) n.m.r. spectroscopy has been developed and applied to various compounds.[1] This technique should be able to give information on molecular conformation, packing, and electron density distribution in the solid state.[2] Therefore, the c.p.m.a.s. technique may be useful particularly for compounds for which single crystals are difficult to obtain. In the initial stage, however, in order to establish the relationship between molecular structure and c.p.m.a.s. data it is very important to compare results of the c.p.m.a.s. technique with those of single-crystal *X*-ray analyses.

Recently Bellitto *et al.*[3–7] reported the preparation and characterization of dithioacetato complexes for Pt, Pd, and Ni for which a variety of structures (monomer, dimer, or linear chain) and oxidation states (+2, +2.5, or +3) are observed, as shown in Figure 1. These compounds have attracted much interest from the viewpoint of solid-state physics and chemistry owing to their low-dimensional nature or/and the unusual oxidation state.[8–10] The dithioacetato ligand is assumed to play a very important role in determining the structure and properties of these compounds.

We have measured the solid-state ^{13}C n.m.r. spectra of $[M_2(S_2CMe)_4]$ (M = Ni, Pd, or Pt), $[M_2(S_2CMe)_4I]$ (M = Ni or Pt), and $[Pt_2(S_2CMe)_4I_2]$ to compare with the solid-state structures, as determined by *X*-ray analysis, and to note the influence of varying metal oxidation state.

Experimental

The compounds were prepared as reported previously.[4–8] A JEOL NM-SH-200 spectrometer (50 MHz for ^{13}C) was used for the n.m.r. measurements. All spectra were obtained using m.a.s. at room temperature. They were generated from 5 000—10 000 scans at a rate of one scan per 10 s, where the contact time was chosen as 1 ms.[2] The methylene carbon of adamantane (+29.5 p.p.m. relative to $SiMe_4$) was used as an external standard. The spectral assignments were made using Opella's method.[11]

Results and Discussion

High-resolution ^{13}C c.p.m.a.s. n.m.r. spectra of $[M_2(S_2CMe)_4]$ (M = Pt, Pd, or Ni) are shown in Figure 2. The methyl and quaternary carbons of the $[Pt_2(S_2CMe)_4]$ complex appeared as singlets at 41.9 and 173.9 p.p.m. respectively, while for $[Ni_2(S_2CMe)_4]$ two methyl signals of equal intensity at 38.9 and 40.9 p.p.m. and a slightly broadened signal for the quaternary carbon at 176.7 p.p.m., are observed. Moreover, the $[Pd_2(S_2CMe)_4]$ complex showed three methyl signals of equal intensity at 41.6, 43.5, and 47.3 p.p.m. and two quaternary signals at 174.6 and 176.0 p.p.m.

According to the *X*-ray structural analyses,[4] the $[Pt_2(S_2CMe)_4]$ complex consists of binuclear units with four bridging ligands as shown in Figure 1(*a*). Strictly speaking, the four methyl groups can be distinguished crystallographically, but the differences are quite small, since the binuclear units have a pseudo-four-fold axis, are stacked in columns along the crystallographic *c* axis, and are far from one another. Therefore, the methyl signal of the $[Pt_2(S_2CMe)_4]$ complex is observed as a single peak.

The $[Ni_2(S_2CMe)_4]$ complex also has the dimeric unit shown in Figure 1(*a*), but here the units are in a 'slipped-stacked' arrangement and there is a Ni···S contact between two adjacent dimers in the unit cell.[7] Accordingly, the complex showed two methyl and a slightly broadened quaternary carbon signal.

The *X*-ray structural analysis for the $[Pd_2(S_2CMe)_4]$ complex indicates mononuclear $Pd(S_2CMe)_2$ and binuclear $Pd_2(S_2CMe)_4$ units which alternate along the crystallographic *a* axis [Figure 1(*b*)].[4] Therefore, this compound is more correctly formulated as $[Pd(S_2CMe)_2][Pd_2(S_2CMe)_4]$. Crystallographically, the binuclear unit has two different types of methyl group and the mononuclear unit has another type of methyl group, which results in three methyl signals in the

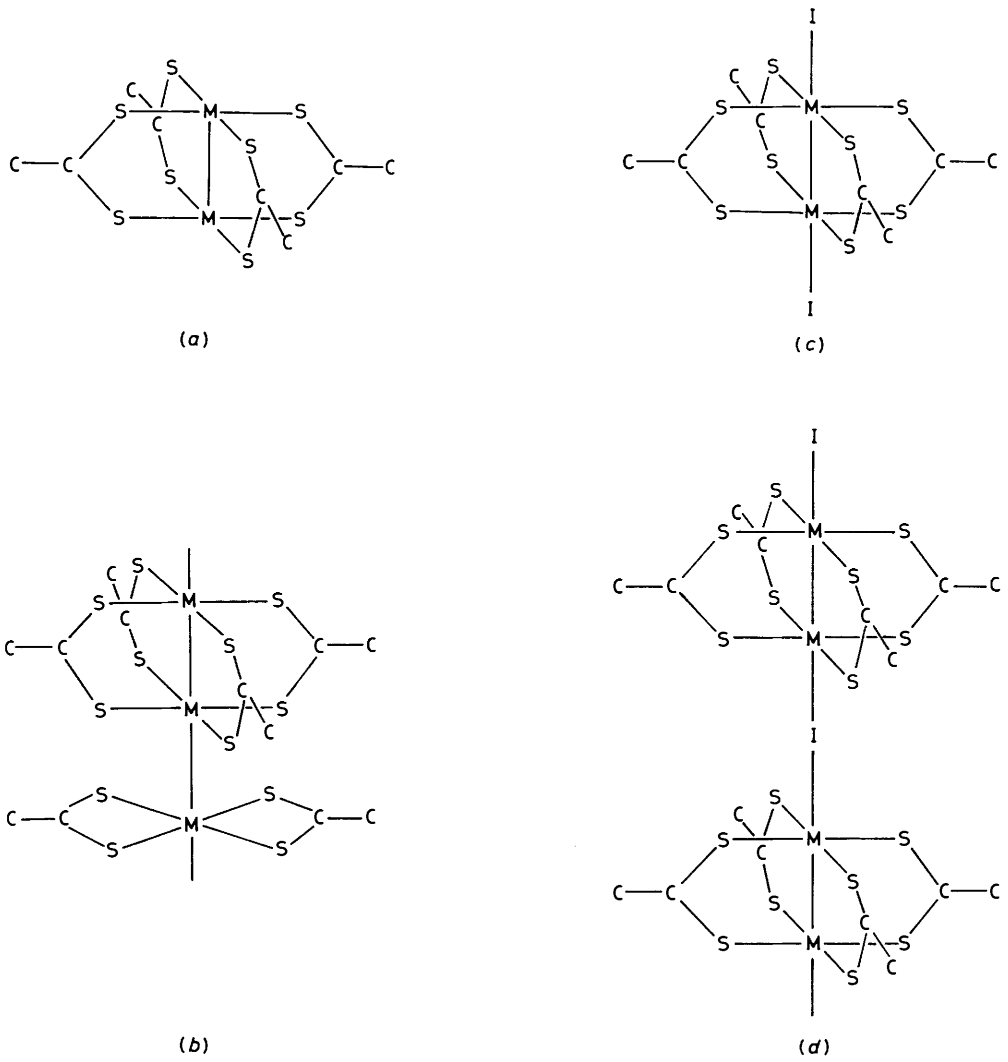

Figure 1. Structures of dithioacetato complexes. (*a*) $[M_2(S_2CMe)_4]$, (*b*) $[M(S_2CMe)_2][M_2(S_2CMe)_4]$, (*c*) $[M_2(S_2CMe)_4I_2]$, and (*d*) $[M_2(S_2CMe)_4I]$

c.p.m.a.s. spectrum [Figure 2(*c*)]. The quaternary carbon signals of the binuclear and mononuclear units appear at 174.6 and 176.0 p.p.m. respectively.

The complex $[Pt_2(S_2CMe)_4I_2]$ is assumed to have a structure as shown in [Figure 1(*c*)], by analogy with the crystal structures of $[Pt_2(S_2CPr^i)_4I_2]$ and $[Pt_2(S_2CCH_2Ph)_4I_2]$.[12] The complex is diamagnetic, containing a single metal–metal bond as expected for a d^7–d^7 system. The c.p.m.a.s. spectrum of the complex showed one methyl and one quaternary carbon signal [Figure 3(*a*)], indicating that the environments of the four S_2CMe ligands in $[Pt_2(S_2CMe)_4I_2]$ are similar. Compared with the spectrum of $[Pt_2(S_2CMe)_4]$ [Figure 2(*a*)], the quaternary carbon signal of $[Pt_2(S_2CMe)_4I_2]$ is shifted to lower field, while the methyl signal is essentially unshifted. The Pt^{3+} ion is assumed to attract electron density from the surrounding quaternary carbon atoms more effectively than does Pt^{2+}.

The c.p.m.a.s. spectrum of the $[Pt_2(S_2CMe)_4I]$ complex showed only two broad methyl signals, at 41.0 and 45.9 p.p.m. while the quaternary carbon signal was not observed in the range -100 to 300 p.p.m. [Figure 3(*b*)]. The crystal structure of the complex is represented in Figure 1(*d*).[6] This shows that the $Pt_2(S_2CMe)_4$ units are stacked with iodo-bridges along the crystallographic *b* axis, so forming a linear chain structure. The complex shows semiconductive behaviour along the chain axis (with a conductivity of 2.0 Ω^{-1} cm^{-1} at room temperature)[13] and the formal oxidation state of the metal is $+2.5$, which leads to one unpaired electron per dimer unit. Although the complex shows a strong antiferromagnetic interaction between unpaired electrons on the dimer units, there remains a slight magnetism at room temperature ($\mu_{eff.} = 0.8$). This presumably leads to broadening of the methyl signals, and the failure to observe the quaternary carbon atom signal in the range -100 to 300 p.p.m.

It is also noticed that two methyl signals were observed for the $[Pt_2(S_2CMe)_4I]$ complex [Figure 3(*b*)], while only one was observed for $[Pt_2(S_2CMe)_4]$ [Figure 2(*a*)]. Since the $Pt_2(S_2CMe)_4I$ units are stacked along the crystallographic *b* axis, peak splitting based on a 'packing effect'[2] is not expected in this system. Hence, the slight magnetism of the complex may emphasize the small crystallographic difference between two methyl group environments in the $[Pt_2(S_2CMe)_4I]$ complex.

Similarly, the c.p.m.a.s. spectrum of $[Ni_2(S_2CMe)_4I]$ showed two broad methyl signals at 23.4 and 30.4 p.p.m. [Figure 3(*c*)].

It is concluded that the c.p.m.a.s. signals of the S_2CMe ligand are influenced by the molecular structure, molecular packing, and oxidation state of the central metal ion.

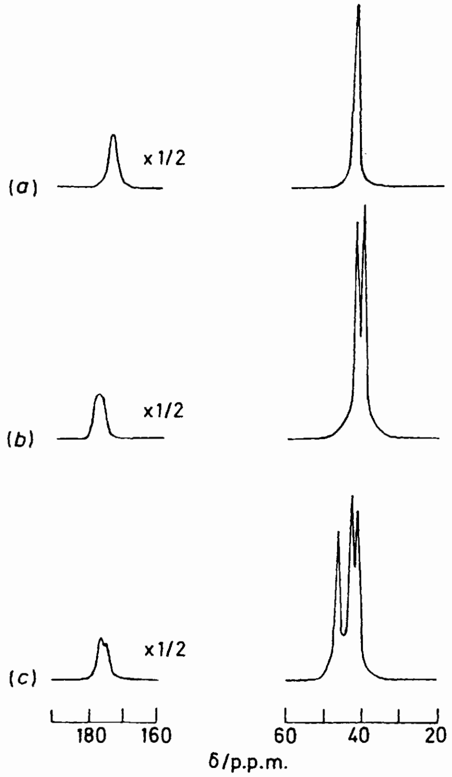

Figure 2. High-resolution ^{13}C c.p.m.a.s. n.m.r. spectra of (*a*) $[Pt_2(S_2CMe)_4]$, (*b*) $[Ni_2(S_2CMe)_4]$, and (*c*) $[Pd(S_2CMe)_2]$-$[Pd_2(S_2CMe)_4]$

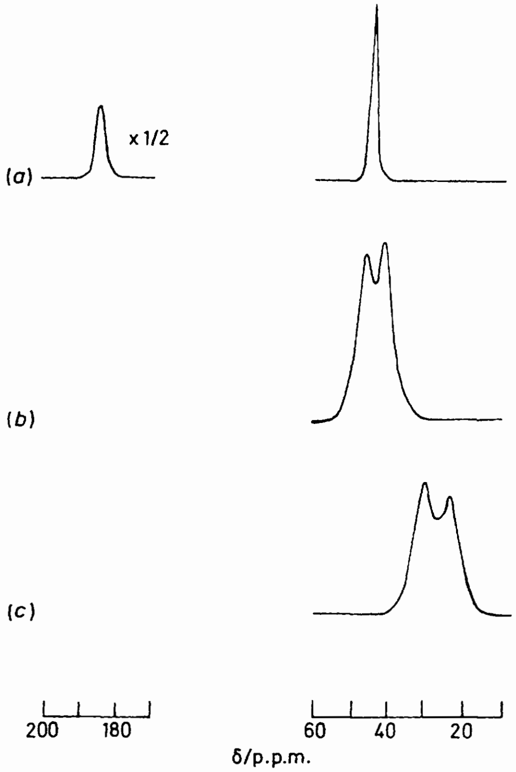

Figure 3. High-resolution ^{13}C c.p.m.a.s. n.m.r. spectra of (*a*) $[Pt_2(S_2CMe)_4I_2]$, (*b*) $[Pt_2(S_2CMe)_4I]$, and (*c*) $[Ni_2(S_2CMe)_4I]$

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