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Ligating Properties of Platinum(I1) Ions in Mixed-Metal (Pt,M) Trimers (M = **Cu(II), Ni(II), Co(II), Fe(I1))**

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Received October 9, *1985*

The electronic reflectance spectra in the range 500–1500 nm of the trimers Cu{(NH₃)₂Pt(1-MeU)₂]₂X₂·nH₂O (X₂ = SO₄, X = NO₃) and Cu{(NH₃)₂Pt(1-MeU)(1-MeC)₁₂(NO₃)₄·6H₂O (1-MeU = 1-methyluracil described. Each trimer contains Cu(I1) ions in a tetragonally elongated octahedral coordination geometry, the axial sites being occupied by **F't(I1)** ions. The "d-d" transition energies and **EPR** parameters of the Cu(I1) ions suggest that the **Pt(I1)** ions effectively function as ligands which, despite their formal positive charge, produce a weak σ -antibonding perturbation on the copper(II) d_r2 orbitals. The angular overlap model is used to quantify this interaction, and it is shown that the transition energies observed in the electronic spectra of analogous trimers formed by Ni(II), Co(II), and Fe(I1) may be reproduced satisfactorily by assuming bonding parameters (reduced slightly in magnitude) identical with those deduced for the corresponding copper(I1) complex.

Introduction

As part of a general investigation of the ligating properties of the pyrimidine nucleobases 1-methylcytosine (1-MeC), 1methylthymine (1-MeT), and 1-methyluracil $(1-MeU)$, we recently prepared a range of novel trimeric complexes of the general form

where $M = Cu(II), Ni(II), Co(II), Fe(II), or Mn(II).$ ^{1b,c,2-4} For the complexes $Mn[Pt(NH_3)_2(1-MeT)_2]_2Cl_2.10H_2O^{1b}$ and Cu- $[Pt(NH₃)₂(1-MeU)(1-MeC)]₂(NO₃)₄·6H₂O³ single-crystal X-ray$ studies have revealed trimeric structures with quite similar dispositions of the metal and ligand atoms. In each case the central metal lies on a crystallographic inversion center, so that the $M(O_4)$ atoms are rigorously coplanar. The terminal Pt(I1) ions complete a distorted octahedral arrangement of atoms about each metal, the Pt-M distance being \sim 270 pm, and it seems very likely that a similar geometry occurs for the other complexes in the series.⁴ The EPR spectrum of the $Mn(II)$ complex² and the Mössbauer spectrum of $Fe[(NH₃)₂Pt(1-MeU)₂]₂(NO₃)₂·5H₂O⁴$ both imply a highly distorted tetragonal ligand environment for the central metal ion, and the electronic spectra of $Ni(II)$, $Co(II)$, and $Fe(II)$ members of the series⁴ have been interpreted as showing that the effective ligand field associated with the axial Pt(I1) ions is quite weak.

There is considerable current interest in metal-metal bonds between transition ions,⁵ and the present series of compounds provides a useful way of probing this kind of interaction. It is well established that metal-metal interactions can have a profound effect on the energy states of solids containing infinite linear chains of d⁸ metal ions separated by distances rather larger than those found in the present trimers.⁶ For instance, the characteristic red color of **bis(dimethylglyoxime)nickel(II),** with Ni-Ni separations of 325 pm, is thought to be caused by absortions associated

with energy levels that are influenced by overlap of the metal 3d,2 and 4p, orbitals,' as are the colors of a range of complexes with similar crystal structure of general formula $(PtA₄)(PtX₄)$, where X is C1 or Br and A is one of several substituted amines and the metal-metal separations are in the range 320–350 pm.⁸ The bonding interactions in the present trimers are of interest for two main reasons. First, they represent chains truncated to a length of three members. Second, each trimer involves two quite different metal ions, and the spectroscopic properties of the central, first-row transition metal are rather similar to those of analogous, six-coordinate complexes, implying that the terminal $Pt(II)$ ions may be thought of as acting as ligands.

Assuming that the Pt(I1) ions may be considered to act as novel, formally positively charged, ligands, it is of interest to determine the nature of their interaction with the central-metal d orbitals. The angular overlap model (AOM) is an especially convenient way of interpreting metal-ligand interactions^{9,10} as the parametrization is carried out in terms of metal-ligand σ - and π -bonding parameters that hopefully are of direct chemical significance. For instance, Gerloch and co-workers recently determined that the e_{τ} parameters of several phosphine ligands are negative, implying that they function as π acceptors,¹¹ in agreement with the simple, qualitative concepts that have long been used to explain the chemical behavior of complexes of these ligands. In particular, when a series of related compounds are involved, the relatively simple spectra observed for a Cu(I1) complex may be interpreted in terms of metal-ligand bonding parameters, which can then be used to predict the energy levels of analogous complexes of other metal ions where interelectron repulsion effects produce much

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Table I. Excited-State Energies and EPR and Structural Parameters of (Pt,Cu) Trimers and Comparison Compounds

 ${}^{\circ}$ Cu[(NH₃)₂Pt(1-MeU)₂]₂(NO₃)₂·6H₂O. ${}^{\circ}$ Cu[(NH₃)₂Pt(1-MeU)₂]₂SO₄·12H₂O. ${}^{\circ}$ Cu[(NH₃)₂Pt(1-MeU)(1-MeC)]₂(NO₃)₄·6H₂O. ${}^{\circ}$ acac = acetylacetonato anion; data from ref 16. *Bis((p-methoxybenzoyl)trifluoroacetonato)copper(II)-2-(1,4-dioxane)*; data from ref 17. *Data from ref* 18 and: Getz, D.; Silver, B. J. Chem. Phys. 1974, 61, 630. ^gA and B refer to assignments of the electronic spectra corresponding to the d-orbital energy sequences $d_{x^2-y^2}$ >> d_{x^2} > d_{xy} > $d_{xx,yz}$ and $d_{x^2-y^2}$ >> d_{xy} > d_{xyz} > d_{x^2} , respectively, as illustrated in Figure 2. * Excited-State energies in cm⁻¹. 'Hyperfine splitting in $cm^{-1} \times 10^4$. 'Experimental value unavailable. k Bond lengths in pm.

Figure 1. Electronic reflectance spectra of (A) Cu $[(NH₃)₂Pt(1 \text{MeU}_{212}(\text{NO}_3)_2.6\text{H}_2\text{O}$, (B) Cu[(NH₃)₂Pt(1-MeU)₂]₂SO₄.12H₂O, and (C) $Cu[(NH₃)₂Pt(1-MeU)(1-MeC)](NO₃)₄·6H₂O.$

more complex spectra. This approach was recently used successfully to interpret the EPR and optical spectra of a number of low-spin $\text{cobalt}(II)$ Schiff base complexes.^{12,13} With this aim in mind, we report here the electronic spectra of typical Cu(II) trimers of the above type. These are analyzed by using a set of metal-ligand bonding parameters which, with minor changes, produce calculated excited-state energies in good agreement with the observed electronic spectra of the analogous Ni(II), Co(II), and Fe(I1) complexes. The results are interpreted in terms of the effective ligand field produced by the Pt(I1) ions at each central metal.

Experimental Section

The preparation and EPR spectra of the complexes $Cu[(NH₃)₂Pt(1 MeC$)(1-MeU)₂(NO₃)₄.6H₂O, Cu[(NH₃)₂Pt(1-MeU)₂]SO₄.12H₂O, and $(NO₃)₂·6H₂O$ have been described previously.³ The electronic spectra (shown in Figure 1) were measured by reflection at 295 K with a Beckman DK2 spectrometer having the standard reflection accessory.

Discussion

The Cu-O bond lengths in Cu $[(NH₃)₂Pt(1-MeC)(1 MeU)$]₂(NO₃)₄.6H₂O are quite similar (193 and 199 pm),³ suggesting approximate tetragonal symmetry for the ligand field, and this is confirmed by the axially symmetric **g** tensor of the complex.³ Three "d-d" transitions are expected for a Cu(I1) complex having effective *D4h* symmetry, and the spectra of the present complexes each show three bands centered at \sim 8600, \sim 11 300, and \sim 14 500

cm⁻¹. In addition, a weak shoulder is observed at \sim 16700 cm⁻¹.
This is tentatively assigned to the formally spin-forbidden ³A_{2g} cm⁻¹. In addition, a weak shoulder is observed at \sim 16700 cm⁻¹.
This is tentatively assigned to the formally spin-forbidden ³A_{2g} \leftarrow ¹A_{1g} transition of the Pt(II) ions, which is expected to occur in this overtones of the ligands and lattice water molecules occur at \sim 6700 and \sim 5000 cm⁻¹, but that the region above \sim 7000 cm⁻¹ is clear of ligand interference.⁴

The "d-d" transition energies and EPR parameters of the three Cu(I1) trimers are compared with those of various tetragonal complexes with oxygen ligands in Table I. These range from the truly four-coordinate, planar complex Egyptian blue,¹⁵ through solid **bis(acetylacetonato)copper(II),** in which weak axial interactions with neighboring ligand π systems may occur,¹⁶ to a dioxane adduct of a bis(acetylacetonato) complex¹⁷ and, finally, the hexaaquacopper (II) ion.¹⁸ It may be seen that the d-orbital energy sequence is $b_{1g}(x^2 - y)^2 \gg a_{1g}(z^2) > b_{2g}(xy) > c_g(xz,yz)$ in every case except Egyptian blue, for which $a_{1g}(z^2)$ is lowest in energy.¹⁵ The former energy sequence is normally expected even for four-coordinate, planar complexes, because of the σ interaction of the d_{z} orbital with the in-plane ligands, and the anomalously low energy of this orbital in Egyptian blue and other planar, four-coordinate complexes is thought to be due to configuration interaction with the $Cu(II)$ 4s orbital.^{19,20}

Two assignments are thus possible for the Pt/Cu trimers—that similar to those complexes with axial ligand coordination(A) and that analogous to Egyptian blue (B) (the third possible assignment, with $a_{1g}(z^2)$ intermediate in energy between $b_{2g}(xy)$ and $e_g(xz,yz)$, is highly unlikely, as it would suggest an unreasonably large π interaction with the ligand oxygen atoms). The former assignment implies a d-orbital energy sequence in the trimers quite similar to that in other tetragonally distorted six-coordinate copper(I1) complexes. This in turn implies that the $Pt(II)$ ions function as essentially normal ligands, with the filled $5d_{z}$ orbitals interacting with the Cu(II) $3d_{z^2}$ orbital. Assignment B, on the other hand, suggests an anomalously low energy for the Cu(II) d_{z} orbital. Simple electrostatic arguments might relate this to the stabilizing effect of the formal positive charge **on** the Pt(I1) "ligands", while **a** simple molecular orbital picture would infer that the dominant interaction is with the empty 6p orbitals of the Pt(I1) ions. **In** effect, assignment A suggests that the Pt(I1) ions function as weak σ donors, while B implies that they act as σ acceptors toward the

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Figure **2.** Schematic diagram showing the way that assignment A or B of the d-orbital energies of the Cu(II) ions in the (Pt₂Cu) trimers may be derived if the dominant interaction is with the filled $Pt(II)$ Sd_z orbital or the empty $6p_z$ orbital, respectively.

 $3d_{z^2}$ Cu(II) orbital; these scenarios are depicted schematically in Figure 2.

Unfortunately, the crystals of each Cu(I1) trimer are too small to allow the measurement of single-crystal polarized electronic spectra, so that this technique cannot be used to help in the band
assignments. The molecular g values of a Cu(II) complex are
conventionally related to the excited-state energies via the
equations
 $g_{\parallel} = 2.002 - \frac{8\lambda k_{\$ assignments. The molecular g values of a $Cu(II)$ complex are conventionally related to the excited-state energies via the equations

$$
g_{\parallel} = 2.002 - \frac{8\lambda k_{\parallel}^2}{E_{xy}}
$$
 (1a)

$$
g_{\parallel} = 2.002 - \frac{8 \lambda K_{\parallel}^{-}}{E_{xy}}
$$
(1a)

$$
g_{\perp} = 2.002 - \frac{2 \lambda k_{\perp}^{2}}{E_{xzyz}}
$$
(1b)

Here, λ is the spin-orbit coupling constant (-829 cm⁻¹ for Cu²⁺), E_{xy} and $E_{xz,yz}$ are the energies of the excited states indicated by the subscripts, and k_{\parallel} and k_{\perp} are the so-called orbital reduction parameters. While it is now accepted that the latter parameters cannot be used to quantify the covalency of a complex,²¹ particularly when ligands with high spin-orbit coupling constants are involved, $2²$ it does seem that there is an approximate relationship between the expected degree of covalency and the deviation of k from unity. For the present trimers the values of k_{\parallel}^2 and k_{\perp}^2 estimated by using eq 1 for both possible assignments of the electronic spectra are given in Table I. It can be seen that assignment A implies reduction parameters for the trimers fairly similar to those observed for the bis(acetylacetonato) complexes, while B suggests parameters significantly lower than those of the other complexes. While the effects of the Pt(I1) ions on the EPR parameters of the trimers are unknown, it seems likely that they are quite small-for instance, the metal hyperfine splittings A_z are consistent with the fact that the observed g values and excited-state energies lie between those of the 1,4-dioxane adduct and hexaaqua complex (Table I). It therefore **seems** that the EPR parameters of the Pt_2Cu trimers suggest that d-orbital energy sequence A is considerably more likely than B.

Assuming **S** interactions to be negligible, the d-orbital energies of a complex of D_{4h} symmetry may conveniently be related to the AOM ligand bonding parameters via eq 2a-d, where the symbols

$$
E(d_{x^2-y^2}) = 3e_{\sigma}(xy) \tag{2a}
$$

$$
E(\mathbf{d}_{z^2}) = e_{\sigma}(xy) + 2e_{\sigma}(z) \tag{2b}
$$

$$
E(\mathbf{d}_{xy}) = 4e_{\pi c}(xy) \tag{2c}
$$

$$
E(d_{xz,yz}) = 2e_{\pi s}(xy) + 2e_{\pi}(z)
$$
 (2d)

 (xy) and (z) specify the in-plane and axial ligands and the subscripts s and c discriminate between the oxygen π orbitals lying in and out of the plane of the nucleobases, respectively. The three transitions energies observed for the Cu(I1) complexes are clearly inadequate to determine all the parameters in eq 2a-d independently. It was therefore assumed initially that the π interaction with the Pt(II) ions is negligible compared with the σ interaction $(e_{\tau}(z) \approx 0.0)$. The inclusion of a small π -antibonding interaction $(e_{\tau}(z) = 250 \text{ cm}^{-1})$ was subsequently found to have only a minor effect on the other AOM parameters. It was further assumed that the aromatic ligands are π donors with $e_{\pi s}(xy) \leq e_{\pi s}(xy)$. This seems reasonable, in view of both the nature of the ligands and the AOM parameters derived from the Cu(I1) complexes of other similar ligands.²³⁻²⁶ The three Pt₂Cu trimers have quite similar electronic spectra, and the AOM parameters derived by using eq 2a-d and assuming each possible assignment, for the limiting situations outlined above, are as follows:

assignment A

$$
e_{\pi s} = e_{\pi c}
$$
: $e_{\sigma}(xy) \approx 5885 \pm 35$, $e_{\pi}(xy) \approx 1600 \pm 100$, $e_{\sigma}(z) \approx 1580 \pm 200$ cm⁻¹

$$
e_{\pi s} = 0.0
$$
: $e_{\sigma}(xy) \approx 4820 \pm 60$, $e_{\pi c}(xy) \approx 1600 \pm 100$,
 $e_{\sigma}(z) \approx 520 \pm 180 \text{ cm}^{-1}$

assignment B

$$
e_{\tau s} = e_{\tau c}
$$
: $e_{\sigma}(xy) \approx 4465 \pm 200$, $e_{\tau}(xy) \approx 1965 \pm 300$,
 $e_{\sigma}(z) \approx -2765 \pm 200$ cm⁻¹

$$
e_{\pi s} = 0.0
$$
: $e_{\sigma}(xy) \approx 3750 \pm 120$, $e_{\pi c}(xy) \approx 1065 \pm 300$,
 $e_{\sigma}(z) \approx -3475 \pm 50 \text{ cm}^{-1}$

The values for the nucleobases may be compared with those of other oxygen donor ligands, which range from $e_a \approx 7400 \text{ cm}^{-1}$ $e_{\pi c} \approx 1700 \text{ cm}^{-1}$ for bis(acetylacetonato)copper(II) complexes²⁷ to $e_{\sigma} \approx 4500 \text{ cm}^{-1}$, $e_{\pi 0} \approx e_{\pi 0} \approx 1500 \text{ cm}^{-1}$ for $\text{Cu}(H_2\text{O})_6{}^{2+28}$ The AOM parameters confirm the qualitative conclusions concerning the nature of the perturbations of the Cu(I1) d orbitals by the Pt(II) ions outlined above. Assignment A, with $e_{\sigma}(z) \approx 1000 \text{ cm}^{-1}$, implies that the Pt(II) groups function as weak σ donors, the magnitude of the interaction being quite similar to that observed for "semicoordinated" ligands in many tetragonally distorted $Cu(II)$ complexes.²⁹ Assignment B, on the other hand, requires the Pt(II) ions to act as moderate σ acceptors, with $e_{\sigma} \approx -3000$ cm⁻¹. It may be noted that the former assignment produces estimates of the bonding parameters of the organic ligands that agree well with those of other oxygen donors toward Cu(II), while the agreement obtained by using assignment B is less **good.**

Assuming that the ligand bonding parameters and d-orbital energies in the trimers formed by other divalent metals are similar to those of the Cu(I1) complexes, the state energies in the former compounds may be estimated by simply adding in the effects of interelectron repulsion. This was done for the series M- $[(NH₃)₂Pt(1-MeU)₂]₂(NO₃)₂·xH₂O (M = Ni, Co, Fe) by using$

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Table II. Observed and Calculated Transition Energies in the Trimers M[(NH₃₎₂Pt(1-MeU)₂](NO₃₎₂.xH₂O

"Calculated by assuming d-orbital energy splittings 90% of those in the analogous Cu(II) complex (see Table I and text), namely $e_q(z) = 5265$ cm^{-1} , $e_{\pi}(xy) = e_{\pi}(xy) = 1377$ cm⁻¹, $e_{\pi}(z) = 1247$ cm⁻¹ for assignment A, and $e_{\pi}(z) = 4179$ cm⁻¹, $e_{\pi}(xy) = e_{\pi}(xy) = 1125$ cm⁻¹, $e_{\pi}(z) = -2342$ cm⁻¹ for assignment B; Racah parameters $B = 850 \text{ cm}^{-1}$, $C = 3570 \text{ cm}^{-1}$. Symmetry designations are indicated in parentheses for the excited states derived from assignment A. The effects of spin-orbit coupling, neglected for the results reported in the table, were also investigated and found to be negligible as far as the overall position of each band is concerned. ^b Treatment identical with that used for the Ni(II) and Fe(II) complexes, except that the AOM parameters were reduced to 80% of the values derived from the spectrum of the Cu(II) complex. ^cRegion obscured by intense absorption. "Infrared overtones prevent band identification in this region.

the computer program **CAMMAG** written by Gerloch and *co*workers³⁰ and assuming both assignments A and B for the electronic spectra of the copper complex. Excellent agreement was obtained with the transition energies observed in the electronic spectra of the Ni(II), Co(II), and Fe(I1) complexes by using assignment A, but with the AOM bonding parameters reduced by 10% for the Ni(I1) and Fe(I1) trimers and 20% for the Co(I1) complex. The use of the AOM parameters derived from assignment B, **on** the other hand, produced poor agreement with the electronic spectra. The Racah parameters were in each case reduced to $\sim80\%$ of the free-ion value, which is consistent with the orbital reduction parameters deduced from the **g** values of the Cu(I1) complex. The transition energies estimated for the complexes by using the two possible d-orbital energy sequences are given in Table 11, together with the reported energies of the band maxima. The assignments in each case concur with those given previously. In the *case* of the peak of moderate intensity observed at 18700 cm^{-1} for the nickel(II) trimer, an ambiguity existed between the assignment of this to the ${}^{3}A_{2g}$ (2)or ${}^{1}E_{g}$ levels; the present study favors the latter. This peak also occurs with a relatively high intensity at a similar energy $(17 300 \text{ cm}^{-1})$ in the highly tetragonally distorted complex [Ni(2-methyl $imidazole)_4Br]Br.³¹$ It was suggested that the high spin-orbit coupling constant of the bromide ligand may contribute to the breakdown of the normal spin-selection rules in this complex, $3¹$ and possibly a similar effect is induced by the platinum(I1) ions

in the nickel(I1) trimer. The remarkably good agreement with the observed electronic spectral transition energies strongly implies that the d-orbital energy sequence A applies generally for the whole series of complexes, with the d-orbital splittings decreasing somewhat in the sequence $Cu(II) > Ni(II) \sim Fe(II) > Co(II)$. A rather similar trend is observed for the d-orbital splittings Δ of the hexaaqua ions, which follow the sequence $Cu(II) > Fe(II)$ $> Ni(II) > Co(II),^{32}$ though it must be remembered that here the $Cu(II)$ complex and, to a lesser extent, the $Fe(II)$ complex have d-orbital splittings enhanced by Jahn-Teller distortions. It is noteworthy that the Mn-0 bond length (213 pm) in Mn- $[(NH₃)₂Pt(1-MeT)₂]₂Cl₂·10H₂O₁^{1b}$ is significantly longer than the Cu-O distance (196 pm) in Cu $[(NH₃)₂Pt(1-MeC)(1 MeU)$]₂(NO₃)₄.6H₂O, which is also consistent with the above trend in metal-ligand interactions. It thus seems that similar metalligand interactions occur with the central M(I1) ions in the whole range of trimers, with the Pt(II) ions functioning as weak σ donors via filled $5d_{r^2}$ orbitals. In effect, therefore, the Pt(II) ions may be thought of as a novel type of ligand that formally carries a positive charge.

Acknowledgment. M.A.H. gratefully acknowledges the receipt of a Humboldt Research Fellowship for the period when part of this research was carried out. **Dr.** M. Gerloch, Inorganic Chemistry Laboratory, University of Cambridge, is thanked for making available a copy of the computer program **CAMMAG.**

Registry No. I, 83434-36-0; 11, **83351-00-2;** 111, **91032-23-4;** Ni- $[(NH₃)₂Pt(1-MeU)₂]₂(NO₃)₂$, 97852-02-3; $Co[(NH₃)₂Pt(1-MeU)₂]₂$ (NO₃)₂, 97851-99-5; $Fe[(NH₃)₂Pt(1-MeU)₂]₂(NO₃)₂$, 97851-95-1.

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