Hexanitrometallates. Part III.[1] Electron Transfer Spectra

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In the complexes $A_2A'M(NO_2)_6$ the region 20—30 × 10^3 cm^{-1} shows a variety of transitions depending on A,A′ and M, in addition to (*d–d*) transitions of M. If the M–N bond is weak and M is not oxidizable or reducible the internal transitions of NO_2^- occur, hardly perturbed from those in $NaNO_2$. If M is Ce^{III}, Bi^{III}, or Pb^{II} electron transfer $[(NO_2^-)_6 \leftarrow M]$ occurs. When A or A′ include Tl^{I}, Ag^{I}, or Pb^{II} and M is optically reducible (Co^{III}, Co^{II}, Fe^{II}, Ni^{II}, or Cu^{II}) one transition $(M \leftarrow A,A')$ is observed. $[M \leftarrow (NO_2^-)_6]$ transitions are seen when M is optically reducible. Electron transfer transitions $(NO_2^- \leftarrow A,A')$ are not observed. In $Cs_2CdCd(NO_2)_6$ doped with Co^{III} and Pb^{II}, which both occupy the M site, no $(Co^{III} \leftarrow Pb^{II})$ electron transfer is observed.

THE class of complexes $A_2A'M(NO_2)_6$ can be prepared with an unusually wide range of A,A′ and M.[2] Stable, well characterized compounds are available with the A site occupied by K^+, Rb^+, Cs^+, Ag^+, or Tl^+; the A′ site occupied by Na^+, Ag^+, Tl^+, Ca^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, or Hg^{2+}; and the M site occupied by Cd^{2+}, Hg^{2+}, Ln^{3+}, Bi^{3+}, dipositive or tripositive transition metal ions. Not all the possible, electrically neutral, compounds have been reported but the range can be extended by doping. For example, pure $Pb(NO_2)_6^{4-}$ and $Mn(NO_2)_6^{4-}$ compounds are unknown but both can be prepared in the white $Cs_2CdCd(NO_2)_6$ host lattice.

The compounds $A_2A'M(NO_2)_6$ have a face-centred cubic structure [2,3] or are tetragonal with only small distortions from the cubic structure.[4,5] M is surrounded by the N atoms of six NO_2^- ions. The site symmetry is ideally T_h but both static and dynamic distortions have been observed.[4-6] A occupies a site of T_d symmetry surrounded by twelve O atoms from twelve different NO_2^- ions. A′ occupies a site of T_h symmetry surrounded by twelve O atoms belonging to six NO_2^- ions.

In the present paper the electronic spectra (5—30 × 10^3 cm^{-1}) of a range of these complexes are reported (Table 1). Where appropriate the spectra show (*d–d*) transitions but the discussion which follows will be restricted to the electron transfer transitions.

EXPERIMENTAL

Pure compounds were prepared by methods described in the literature [5,7] modified where appropriate to give caesium or thallium salts. All preparations involving cobalt(II) or iron(II) were carried out under oxygen-free nitrogen to avoid contamination with oxidized products.

TABLE 1

Spectra of $A_2A'M(NO_2)_6$, band maxima in 10^3 cm^{-1}

A	A′	M	
Cs	Ag	La	24, 28·5, 30·5
Cs	Na	Y	24, 28·7, 30·0
Tl	Cd	Cd	23, 28·5, 30·0
Cs	Cd	Cd	24, 29·0, 34·0
Cs	Hg	Hg	22·5, 27·7, 31·0
K	Ba	Fe	22, 25·5, 31·6
K	Pb	Fe	20·5, 25·5, 30·3
Cs	Ba	Co	8·6, (13), 16·7, 23·0, 26·0, 30
Cs	Pb	Co	8·8, (13), (16·5), (19·2), 23·0, 26·0, 30
Tl	Ba	Co	8·8, (13), (16·0), 20, (22·5), 25, 30
Cs	Ba	Ni	(10·9), 13·6, 21·3, 30
Cs	Pb	Ni	(10·8), 13·7, 21·7, (26·6), 30
Tl	Ba	Ni	(10·8), 13·5, 20·3, (27·5), 30
Cs	Ba	Cu	16·2, (21·5), 24·5, 29·4
Cs	Pb	Cu	16·4, 19, 24·5, 29·5
Tl	Ba	Cu	16·4, (19), 24·5, 29·5
Cs	Na	Bi	22·8, 27·8, 30·5
Cs	Cd	Cd + Pb	21·7, 26, 29·5, 34
Cs	Hg	Hg + Pb	21·0, 26·0, 30·0, (33)
Cs	Cd + Na	Cd + Co^{III}	(21·4), 26·2, 29·5, (33)
Cs	Cd + Ag	Cd + Co^{III}	21·0, 26·0, 29·5, (34)
Cs	Cd + Tl	Cd + Co^{III}	(22·0), 25·4, 29·5, (34)
Cs	Cd + Na	Cd + Co^{III} + Pb	21·0, 26·0, 29·5, (34)

Doped samples were prepared by adding *ca.* 5 mol % of lead(II) nitrate or sodium hexanitrocobaltate(III) to solutions of cadmium nitrate or mercury(II) nitrate in saturated sodium nitrite. The complex was precipitated by adding caesium nitrate solution to which had been added, if required, thallium(I) nitrate or silver nitrate. The products were well formed cubes of edge 10—30 μm, which appeared homogeneous under the microscope and in *X*-ray powder

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[1] Part II, J. C. Barnes, *Nature*, 1971, **234**, 99.

[2] R. W. G. Wyckoff, ' Crystal Structures,' Interscience, 1965, vol. 3, p. 376.

[3] J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, 1966, **5**, 514.

[4] J. A. Bertrand, D. A. Carpenter, and A. R. Kalyanarama, *Inorg. Chim. Acta*, 1971, **5**, 113.

[5] H. Elliot, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, 1966, **5**, 669.

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[7] A. Ferrari, B. Alessandro, and C. Colla, *Gazzetta*, 1935, **65**, 797.

patterns. Further details of the doped samples listed in Table 1 will be presented separately as part of a wider study of doped $A_2A'M(NO_2)_6$ compounds.[8]

Diffuse reflectance spectra were recorded at room temperature using a Unicam SP 735 spectrophotometer. Pure compounds were diluted with alumina but the doped samples were recorded without dilution. The spectra of a number of the samples were also recorded at 77 K. No more than a marginal improvement in resolution was obtained.

DISCUSSION

Barnes and Peacock[9] have interpreted the spectra of $Cs_2NaLn(NO_2)_6$ by assuming only weak interaction between M and $(NO_2^-)_6$. The region 20—50 × 10^3 cm^{-1} shows the characteristic spectrum of nitrite ion, only slightly perturbed from that of sodium nitrite [Table 2(a)]. Electron transfer transitions appear at low energy if M is readily reducible or readily oxidizable, as in yellow $Cs_2NaCe(NO_2)_6$.[9]

TABLE 2

(a) Spectrum of NO_2^-

	Energy/10^3 cm^{-1}	ε
${}^3B_1 \longleftarrow {}^1A_1$, $(b_1^* \longleftarrow a_1^*)$	22·5	10^{-2}
${}^1B_1 \longleftarrow {}^1A_1$, $(b_1^* \longleftarrow a_1^*)$	27	28
${}^1A_2 \longleftarrow {}^1A_1$, $(b_1^* \longleftarrow a_2)$	34	9
${}^1A_2 \longleftarrow {}^1A_1$, $(b_1^* \longleftarrow b_2)$	46	5000

Data and notation from K. L. McEwen, *J. Chem. Phys.*, 1961, **34**, 547; and W. C. Allen and R. N. Dixon, *Trans. Faraday Soc.*, 1969, **65**, 1168.

(b) Predicted spectrum for $M(NO_2)_6^{n-}$ with strong M–N interaction; K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, 1967, **6**, 562

	Energy/10^3 cm^{-1}	
$3e_g \longleftarrow a_u,e_u$	20—23	Forbidden $[M \longleftarrow (NO_2^-)_6]$
$5t_u \longleftarrow 4t_g$	24—25	Two allowed $[(NO_2^-)_6 \longleftarrow M]$
$3e_g \longleftarrow 4t_u$	40—50	Two allowed $[M \longleftarrow (NO_2^-)_6]$

Caulton and Fenske[10] discussed the case of strong $M-(NO_2^-)_6$ interaction. They predicted that the energy levels of nitrite ion will be so altered that the transitions corresponding to Table 2(a) would occur only at very high energy. The 20—50 × 10^3 cm^{-1} region would contain the electron transfer transitions listed in Table 2(b). The lowest energy allowed band is expected to be a metal to ligand, $[(NO_2^-)_6 \longleftarrow M]$ transition $(5t_u \longleftarrow 4t_g)$. These workers interpreted the spectra of some cobalt(III), cobalt(II), iron(II), and rhodium(III) complexes in terms of their molecular orbital scheme.

In either model the introduction of oxidizable ions to the A or A′ sites raises the possibility of electron transfer from these ions to nitrite or to M.

With other ligands it is sometimes possible to correlate electron transfer spectra with the appropriate half-cell potentials for the metal ions.[11-14] It has been observed that a difference of 1 eV between corresponding transitions in ML_n and $M'L_n$ is associated with a difference of 1 V in the half-cell potentials of M and M′. For the relationship to hold the potentials used must be those for the oxidation or reduction of ML_n and $M'L_n$. This is particularly important for systems such as Fe^{III}/Fe^{II}, Co^{III}/Co^{II}, and Cu^{II}/Cu^{I} where the potential varies widely with the environment of the metal ion. No potentials have been reported for $M(NO_2)_6^{n-}$ complexes, because of the instability of these complexes in solution and because nitrite ion itself can be oxidized or reduced in aqueous solution. There is no justification for seeking more than a qualitative correlation between half-cell potentials in other media and the electron transfer spectra of hexanitrometallates of transition metals. A semi-quantitative relationship is observed (see below) for the complexes of bismuth(III), cerium(III), lead(II), and thallium(I); the oxidation potentials of these ions are less sensitive to changes of environment.

The best alternative correlation for electron transfer spectra requires electron affinities and ionization potentials for nitrite ion and for the metal ions in the $A_2A'M(NO_2)_6$ complexes.[15] No data are available and the need for a strong interaction model and a weak interaction model for bonding in these complexes suggests that the electron affinity and ionization potential for $(NO_2^-)_6$ will vary markedly with M.

At the present time the assignment of the spectra of $A_2A'M(NO_2)_6$ must rely very largely on the changes observed as A,A′ and M are changed. The spectra will be discussed in groups.

No change of Oxidation State Possible for A,A′ *or* M.—The spectra of $Cs_2NaY(NO_2)_6$, $Cs_2CdCd(NO_2)_6$, and $Cs_2HgHg(NO_2)_6$ are all similar to that of $Cs_2NaLa(NO_2)_6$,[9] [Figure 1(a)]. The transitions are those of NO_2^- essentially unperturbed by complex formation. The band at 23 × 10^3 cm^{-1} shows some vibrational structure in each case. The additional intensity seen in this singlet to triplet $(T \longleftarrow S)$ transition compared with sodium nitrite may be due to a spin–orbit coupling mechanism involving the heavy M atom.[16-18]

An Oxidizable Metal Ion Occupies the M *Site.*—Both the weak interaction and the strong interaction models predict a transition $[(NO_2^-)_6 \longleftarrow M]$ at low energy. Apart from those containing transition metal ions (see below), the best characterized complexes of this class are the yellow $Cs_2NaCe(NO_2)_6$[9] and $A_2A'Bi(NO_2)_6$. The latter show intense absorption bands at 22·8 and 27·8 × 10^3 cm^{-1} [Figure 1(b)].

No pure $A_2A'Pb(NO_2)_6$ complexes have yet been reported but lead(II) can be introduced into the $Cs_2CdCd(NO_2)_6$, $Cs_2HgHg(NO_2)_6$, and $Cs_2NaLa(NO_2)_6$ host lattices. These doped samples show bands at 21—22 and 26 × 10^3

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[8] J. C. Barnes and C. S. Duncan, to be presented.

[9] J. C. Barnes and R. D. Peacock, *J. Chem. Soc.* (*A*), 1971, 558.

[10] K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, 1967, **6**, 562.

[11] F. S. Dainton, *J. Chem. Soc.*, 1952, 1533.

[12] J. C. Barnes and P. Day, *J. Chem. Soc.*, 1964, 3886.

[13] J. H. Miles, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1595.

[14] L. G. Nugent, R. D. Baybarz, L. J. Burnett, and J. L. Ryan, *J. Inorg. Nuclear Chem.*, in the press.

[15] M. R. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[16] H. J. Maria, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, 1968, **48**, 4694.

[17] H. J. Maria, A. Wahlborg, and S. P. McGlynn, *J. Chem. Phys.*, 1968, **49**, 4925.

[18] H. J. Maria, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, 1969, **50**, 2777.

cm^{-1} which are not present in lead-free samples. The intensity of these bands increases with increasing lead concentration. These spectra suggest that lead occupies the *N*-co-ordinated M site in these host lattices. There is no absorption assignable to lead at 21 × 10^3 cm^{-1} in $Cs_2PbNi(NO_2)_6$ where lead occupies the *O*-co-ordinated A′ site. Also solution complexes of lead(II) and nitrite, which are *N*-co-ordinated, absorb at 22·8 × 10^3 cm^{-1}.[16,17] (The 26 × 10^3 cm^{-1} region was obscured by the large excess of nitrite present in solution.)

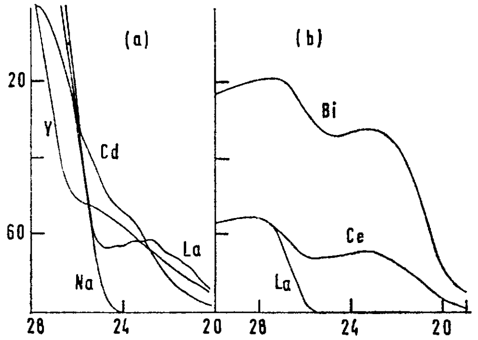

FIGURE 1 Reflectance spectra of hexanitrometallate complexes. Samples were diluted with Al_2O_3 and ground uniformly. (a) Concentration 39·2 mg NO_2^- per 100 mg sample. $Cs_2NaLa(NO_2)_6$, $Cs_2NaY(NO_2)_6^-$, $Cs_2CdCd(NO_2)_6$, $NaNO_2$; (b) Concentration 2·1 mg NO_2^- per 100 mg sample. $Cs_2NaLa(NO_2)_6$, $CsNaCe(NO_2)_6$, $CsNaBi(NO_2)_6$

The bands at 21—23 × 10^3 cm^{-1} in the cerium(III), bismuth(III), and lead(II) complexes are 10—100 fold more intense than those in pure $Cs_2NaLa(NO_2)_6$ or $Cs_2CdCd(NO_2)_6$. The vibrational structure observed on the ($T \longleftarrow S$) transition in the host lattices is not seen when the oxidizable metal ions are present (Figure 1).

The assignment of the 21—22 and 26—27 × 10^3 cm^{-1} bands in $Cd(NO_2)_6^{3-}$, $Pb(NO_2)_6^{4-}$, and $Bi(NO_2)_6^{3-}$ to electron transfer [$(NO_2)_6 \longleftarrow M$], that is the promotion of an *s* (or *f*) electron from M to the $5t_u$ orbital of $(NO_2^-)_6$, is consistent with the very similar oxidation potentials of these metal ions. Extrapolation from these potentials indicates the corresponding transition in $Sn(NO_2)_6^{4-}$ would be expected *ca.* 11 × 10^3 cm^{-1} (Figure 2). When electron transfer transitions are predicted at such low energies the result is often a complete redox reaction rather than an electron transfer absorption followed by reversion to the original ground state. A familiar example is $Cu^{2+} + 2I^- \longrightarrow CuI + \frac{1}{2}I_2$. No hexanitro-complexes of tin(II) have been characterized. Addition of a tin(II) salt to a nitrite solution produces immediate effervescence. It seems likely that the initial step in this reaction involves reduction of nitrite by tin(II).

The oxidation potentials of thallium(I) and silver(I) suggest [$(NO_2^-)_6 \longleftarrow M$] transitions at *ca.* 20 and 26 × 10^3 cm^{-1} respectively (Figure 2). Both these metals form *N*-bonded nitrite complexes in solution but since singly charged ions cannot occupy the M site in solid $A_2A'M(NO_2)_6$ they are restricted to the *O*-co-ordinated sites in these compounds. McGlynne and co-workers[16-18] have reported that nitrite solutions of thallium(I), silver(I), and cadmium(II) show absorption maxima at 21·9 × 10^3 cm^{-1} (ε 0·64), 22·2 × 10^3 cm^{-1} (ε very low), and 23·4 × 10^3 cm^{-1} (ε 0·02) respectively. They assign these transitions to the ($T \longleftarrow S$) absorption of nitrite enhanced by spin–orbit coupling with the metal. Luminescence measurements have confirmed that the ($T \longleftarrow S$) transition occurs at 21—23 × 10^3 cm^{-1} in these complexes.[17,18] The present authors suggest that the greater intensity of absorption in the thallium solutions is associated with the [$(NO_2^-) \longleftarrow M$] transition fortuitously occurring at similar energy to the ($T \longleftarrow S$) absorption. Solution spectra of silver nitrite complexes have not been examined in the 26 × 10^3 cm^{-1} region, where the [$(NO_2^-) \longleftarrow Ag$] transition is expected to occur.

An alternative assignment describes the transitions at 22 and 26 × 10^3 cm^{-1} in nitrite complexes of bismuth(III), lead(II), and thallium(I) as the triplet and singlet ($sp \longleftarrow s^2$) transitions. The present authors reject this assignment. In well-characterized ($sp \longleftarrow s^2$) spectra the singlet transition is found 11—15 × 10^3 cm^{-1} higher in energy than the triplet. The two bands in the nitrite complexes are separated by only 4 × 10^3 cm^{-1}. Again, when ($sp \longleftarrow s^2$) transitions occur at low energy they are found in the order Bi < Pb < Tl, spread over some 10 × 10^3 cm^{-1}. In the nitrite complexes the order is Tl, Pb < Bi, with a spread of only 2·5 × 10^3 cm^{-1}. Ligand effects in ($sp \longleftarrow s^2$) spectra are similar to those described by the nephelauxetic series.[19,20] The ($sp \longleftarrow s^2$) transitions in *N*-co-ordinated nitrite complexes should

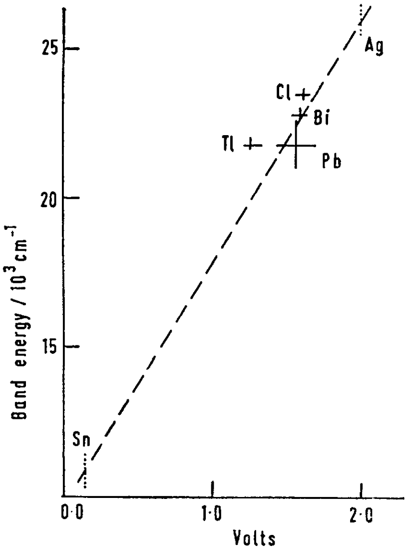

FIGURE 2 Correlation of [$(NO_2^-)_6 \longleftarrow M$] electron transfer band energy with the oxidation potential of M. The dotted line has the slope of 8300 cm^{-1} per volt derived from studies on other systems

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[19] C. K. Jørgensen, ‘Oxidation Numbers and Oxidation States,’ Springer, Berlin, 1969, p. 129.

[20] J. A. Duffy and M. D. Ingram, *J. Chem. Phys.*, 1971, **54**, 443.

lie above those of the chloro-complex, that is above $30{\cdot}5 \times 10^3$ cm^{-1} (Bi), $36{\cdot}8 \times 10^3$ cm^{-1} (Pb), or $40{\cdot}5 \times 10^3$ cm^{-1} (Tl). These bands are not observed. They may be concealed by ligand absorption above 30×10^3 cm^{-1}.

A *or* A′ *Oxidizable,* M *not Reducible.*—$Tl_2CdCd(NO_2)_6$ and $Cs_2AgLa(NO_2)_6$ have spectra very similar to those of $CsCdCd(NO_2)_6$ and $Cs_2NaLa(NO_2)_6$. There is no additional absorption which could be assigned to electron transfer from thallium(I) or silver(I) to the oxygen atoms of nitrite. The spectra of $Cs_2PbM(NO_2)_6$ differ from those of $Cs_2BaM(NO_2)_6$ (M is Co^{II}, Ni^{II}, or Cu^{II}) only in the existence of one extra band. This band is assigned to electron transfer (M $\longleftarrow$ Pb) and not (NO_2^- $\longleftarrow$ Pb) because the energy of the transition varies with M (see below).

A *or* A′ *Oxidizable,* M *Reducible.*—The most probable assignment of any additional features present in the spectrum of, for example, $Tl_2BaM(NO_2)_6$ which do not occur in $Cs_2BaM(NO_2)_6$ is electron transfer (M $\longleftarrow$ Tl).

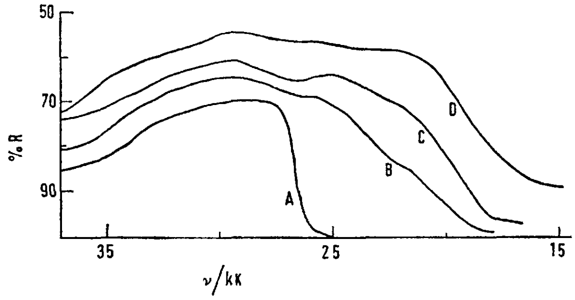

FIGURE 3 Spectra of $Co(NO_2)_6^{3-}$ complexes in $Cs_2CdCd(NO_2)_6$ A $Cs_2CdCd(NO_2)_6$ host lattice; B Host lattice doped with $Co(NO_2)_6^{3-}$ and Na^+; C host lattice doped with $Co(NO_2)_6^{3-}$ and Tl^+. D host lattice doped with $Co(NO_2)_6^{3-}$ and Ag^+. All samples were diluted with Al_2O_3. Curves B, C, and D are displaced vertically for clarity

There are relatively few descriptions of electron transfer between ions of different metals.[15,21] Jørgensen [22,23] found that the spectra of Tl_2IrCl_6 and Ag_2IrCl_6, and similar salts of $OsCl_6^{2-}$, and $OsBr_6^{2-}$ and $ReCl_6^{2-}$, show an additional absorption band lying 4—6×10^3 cm^{-1} below the first allowed transition in the corresponding potassium salts. In each case the band in the silver salt occurred *ca.* 1000 cm^{-1} below that of the thallium salt. Similar observations have been made on a series of chromates.[22] These additional bands were assigned to electron transfer (complex $\longleftarrow$ Tl, Ag). The accepting orbital was largely but not completely localized on the metal atom of the complex. Braterman [24] observed a similar process in transition metal ferrocyanides, where electron transfer occurred from $Fe(CN)_6^{4-}$ to M^{II} for cobalt, nickel, and copper but not for zinc or manganese.

Figure 3 shows the spectra of samples of $Cs_2CdCd(NO_2)_6$ doped with $Co(NO_2)_6^{3-}$ and with either Na^+ or Ag^+ or Tl^+. An additional band appears in the silver and thallium containing samples, lying $3{\cdot}4 \times 10^3$ cm^{-1} (Tl) and $5{\cdot}0 \times 10^3$ cm^{-1} (Ag) lower in energy than the first allowed transition of $Co(NO_2)_6^{3-}$. These bands must represent transitions (Co^{III} $\longleftarrow$ Tl, Ag). Only one transition is possible, electron transfer to low spin Co^{III} must give the excited state of Co^{II}, $t_{2g}{}^6e_g{}^1$ (^2E_g).

$Cs_2PbM(NO_2)_6$ and $Tl_2BaM(NO_2)_6$ each show only one absorption band below 30×10^3 cm^{-1} which is not present in $Cs_2BaM(NO_2)_6$ (M = Ni^{II}, Co^{II}, and Cu^{II}). $K_2PbFe(NO_2)_6$ shows one band not present in $K_2BaFe(NO_2)_6$. For each of these hexanitrometallates only one (M $\longleftarrow$ A,A′) transition is possible. The ground state of A,A′ (s^2) loses an electron to give the excited state (s^1) and the configurations for M are:

Ground state	Excited state
Fe^{II}, $t_{2g}{}^6$	Fe^{I}, $t_{2g}{}^6e_g{}^1$ (^2E_g)
Co^{II}, $t_{2g}{}^6e_g{}^1$	Co^{I}, $t_{2g}{}^6e_g{}^2$ ($^3A_{2g}$)
Ni^{II}, $t_{2g}{}^6e_g{}^2$	Ni^{I}, $t_{2g}{}^6e_g{}^3$ (^2E_g)
Cu^{II}, $t_{2g}{}^6e_g{}^3$	Cu^{I}, $t^2{}_g{}^6e_g{}^4$ ($^1A_{1g}$)

For a given M the transitions from thallium(I) and from lead(II) are seen at very similar energies. The bands occur in the order Co^{II}, Cu^{II} (19×10^3 cm^{-1}) < Fe^{II} ($20{\cdot}5 \times 10^3$ cm^{-1}) < Ni^{II} (27×10^3 cm^{-1}).

In the hexacyanoferrates [24] transitions assigned as [M $\longleftarrow$ $Fe(CN)_6^{4-}$] were reported at $19{\cdot}5 \times 10^3$ cm^{-1} (Cu^{II}) and $33{\cdot}6 \times 10^3$ cm^{-1} (Ni^{II}). The data for Co^{II} cannot be used for comparison because the cobalt ion is high spin in the ferrocyanide but low spin in $Co(NO_2)_6^{4-}$.

When $Cs_2CdCd(NO_2)_6$ was doped simultaneously with hexanitrocobaltate(III), with lead(II), and with sodium ion the spectrum of the product showed only transitions assigned to either $Co(NO_2)_6^{3-}$ or to $Pb(NO_2)_6^{4-}$. Both cobalt(III) and lead(II) occupy M sites in this host lattice. Electron transfer (Co^{III} $\longleftarrow$ Pb^{II}) would involve transfer of an electron by way of two nitrite ions and an intervening A (A′) site.

Using the classification of Robin and Day the last example represents a Class 1 system, for which no interaction spectrum would be anticipated. The (M $\longleftarrow$ A,A′) transitions through a single nitrite bridge are typical of Class 2, and similar to the familiar example of Prussian Blue.

M *Is a Transition Metal Ion,* A *and* A′ *not Oxidizable.*—The spectra of this class are by far the most difficult to interpret. For $Co(NO_2)_6^{4-}$ and $Cu(NO_2)_6^{4-}$ even the number of bands between 15 and 30×10^3 cm^{-1} is in dispute. The spectra in Table 1 combine features observed by other workers without agreeing in detail with either of the published spectra.[5,10] Since redox potentials cannot be used to confirm assignments the comments given here must remain tentative.

The lowest energy allowed transition in the scheme propounded by Caulton and Fenske [10] represents electron transfer [$(NO_2^-)_6$ $\longleftarrow$ M]. It is a weakness of this assignment that this suggests that cobalt(III) and copper(II) should be more readily oxidized than reduced. Again, Mn^{II} is usually readily oxidized but Mn^{II} doped into $Cs_2CdCd(NO_2)_6$ shows no intense absorption below 35×10^3 cm^{-1}.

[21] G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 357.

[22] C. K. Jørgensen, *Acta Chem. Scand.*, 1963, **17**, 1034.

[23] C. K. Jørgensen, *Mol. Phys.*, 1961, **4**, 235.

[24] P. S. Bratermann, *J. Chem. Soc.* (*A*), 1966, 1471.

Since Co^{III}, Co^{II}, Fe^{II}, Ni^{II}, and Cu^{II} act as optical electron acceptors from Tl^{I}, Ag^{I}, or Pb^{II} it seems likely that $[M(3e_g) \longleftarrow (NO_2^-)_6]$ transitions will occur at low energy. If the $A_2A'M(NO_2)_6$ system behaves like A_2IrCl_6, the lowest lying nitrite to metal transition will be found 4—6 × 10^3 cm^{-1} higher in energy than the $(M \longleftarrow Tl^I)$ transition, that is *ca.* 25 × 10^3 cm^{-1} for Fe^{II}, 24 × 10^3 cm^{-1} for Co^{II}, 26 × 10^3 cm^{-1} for Co^{III}, 32 × 10^3 cm^{-1} for Ni^{II}, and 24 × 10^3 cm^{-1} for Cu^{II}. In each case there is a band close to the predicted energy.

CONCLUSIONS

The weak interaction model has been shown to be consistent with the spectra of $La(NO_2)_6^{3-}$, $Cd(NO_2)_6^{4-}$, and $Hg(NO_2)_6^{4-}$.

The interpretations of the spectra of $Bi(NO_2)_6^{3-}$, $Pb(NO_2)_6^{4-}$, and $Ce(NO_2)_6^{3-}$ as $(NO_2^- \longleftarrow M)$ electron transfer and of bands in the spectra of thallium(I), silver(I), and lead(II) hexanitrometallates as $(M \longleftarrow A,A')$ electron transfer are consistent with either model.

Doubt has been thrown on the assignment of the spectra of hexanitro-transition metal complexes by the strong interaction model even in the case of hexanitritocobaltate(III) where the spectrum is not consistent with weak interaction.

There is need for a new model for these spectra in which the covalency of the M–N bond and the relative electron affinity and ionization potential of M are introduced as disposable parameters.

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