The Role of Electronic Delocalization over the Chelate Ring in stabilizing Complexes of 2,2′-Bipyridyl

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The ligand-field spectra of $[ML_3]$ complexes have been recorded [$M = Co^{II}, Co^{III}$, or Ni^{II}; L = 2,2′-bipyridyl (bipy), 2-aminomethylpyridine (amp), and ethylenediamine (en)]. The positions of the bands in the spectra of the 2 amp complexes are the means of the positions of the same bands in the analogous bipy and en complexes, suggesting that electronic delocalization over the chelate ring is not of importance in producing the high position of bipy in the spectrochemical series. A model of the chelate effect is used to support this finding. The significance of the crossover of the $^3T_{2g}$ and ^1E_g energy levels in the nickel(II) complexes is discussed in relation to the problem of assigning the $^3A_{2g}\rightarrow{}^3T_{2g}$ and $^3A_{2g}\rightarrow{}^1E_g$ transitions.

IN a recent paper [1] it was pointed out that the formation constants of ethylenediamine (en) complexes could be related to the formation constants of the analogous ammonia complexes by an equation of the type (1). The log 55.5 term is derived from the asymmetry of the standard reference state,[2] while the factor of 1.152 takes into account the inductive effect of the ethylene bridge in en complexes, which is not present in the analogous ammonia complexes. One might expect that a similar equation (2) would have similar success in relating the

$$\log K_1(\mathrm{en}) = 1.152 \log \beta_2(\mathrm{NH_3}) + \log 55.5 \qquad (1)$$

$$\log K_1(\mathrm{bipy}) = \log \beta_2(\mathrm{py}) + \log 55.5 \qquad (2)$$

stability of complexes of 2,2′-bipyridyl (bipy) to the stability of analogous pyridine (py) complexes. Equation (2) underestimates the stability of bipy complexes by as much as three log units. The failure of equation (2) is at first sight not surprising. Ammonia is only slightly lower than en in the spectrochemical series, with an *f* value (from Jørgensen's [3] $fg = 10Dq$, the ligand-field splitting parameter) of 1.25 as compared with 1.28 for en, which small difference can be attributed to the inductive effect of the ethylene bridge. In contrast, *f* for py is 1.25, but for bipy is *ca.* 1.43.[3] A reasonable explanation [4,5] for the large difference in *f* between py and bipy is that in complexes of bipy electronic delocalization over the chelate ring is able to take place over the carbon–carbon bond joining the two pyridyl groups, which is not possible in py complexes. The ligand 2-aminomethylpyri-

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[1] R. D. Hancock and F. Marsicano, *J.C.S. Dalton*, 1976, 1096.

[2] A. W. Adamson, *J. Amer. Chem. Soc.*, 1954, **76**, 1578.

[3] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon Press, Oxford, 1962.

[4] S. M. Nelson, *M.T.P. Internat. Rev. Sci.*, *Sec.* 5, ed. D. W. A. Sharp, Butterworths, London, 1972, p. 198.

[5] L. F. Lindoy and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1967, **2**, 173.

dine (amp) also contains a pyridyl group capable of co-ordinating to metal ions, but, because of the methylene group between it and the primary amine donor atom, delocalization over the ring, as is theoretically possible in bipy complexes, cannot occur.

If electronic delocalization [4,5] is important in producing the difference between bipy and py complexes, *f* for amp complexes should be close to *f* for en complexes. We have therefore recorded the ligand-field (l.f.) spectra of several amp complexes, and, for comparison, of the analogous bipy and en complexes.

EXPERIMENTAL

All the complexes were prepared as the nitrates from E. Merck guaranteed metal nitrate salts. The cobalt(III) complexes were prepared as the solids, which gave satisfactory C, H, and N elemental analyses for $[Co(en)_3][NO_3]_3$, $[Co(amp)_3][NO_3]_3 \cdot H_2O$, and $[Co(bipy)_3][NO_3]_3 \cdot 3H_2O$. The method used for all three complexes was that described [6] for the en complex. The complexes of Co^{II}, Ni^{II}, and Fe^{II} were prepared in solution by addition of the calculated quantity of the ligand, *ca.* 25% methanol being added to solutions of the bipy and pyridine-2-carboxylic acid (pyca) complexes in order to prevent precipitation. Deoxygenated water was used for the complexes of Fe^{II} and Co^{II} in order to prevent their oxidation. The ligand amp was obtained from Aldrich Chemicals, and bipy, pyca, and en from E. Merck. Oxalic acid was supplied by B.D.H. The ligands were used without further purification to make up 0.1 mol dm^{-3} solutions of the complex, the calculated quantity of Na[OH] being added to deprotonate the carboxylic acid groups of pyca and oxalate. Spectra of the 0.1 mol dm^{-3} complex solutions were recorded on Beckmann Acta CIII and DK2A and on Cary 14 spectrophotometers.

RESULTS

Cobalt(III) *Spectra.*—The large charge-transfer (c.t.) bands found in bipy and, to a lesser extent, in amp complexes mean that, at best, only the lower-energy l.f. bands can be observed, and then often only as shoulders. In $[Co(bipy)_3]^{3+}$ the transition to $^1T_{2g}$ was completely obscured, and that to $^1T_{1g}$ occurred as a shoulder. We are indebted to a referee for suggesting that the latter band could be resolved by assuming that the tail of the c.t. band was exponential in shape. A plot of log absorbance against wavenumber was linear except for the region of overlap of the desired band. Subtraction of the antilogarithms of the least-squares line fitted to the linear portion of the plot from the observed absorbances produced a typical skew-Gaussian band, as observed for the transition $^1A_{1g} \rightarrow {}^1T_{1g}$ in the en and amp complexes of Co^{III}. The band maxima and l.f. parameters for the cobalt(III) complexes studied are as follows (units are cm^{-1}):

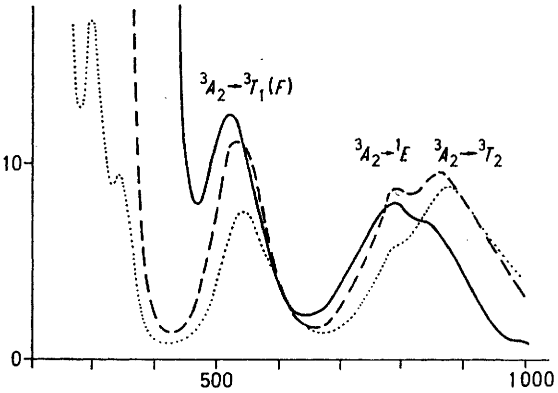
Excited state and l.f. parameters	$[Co(bipy)_3]^{3+}$	$[Co(amp)_3]^{3+}$	$[Co(en)_3]^{3+}$
$^1T_2$		30 200 *	29 700
$^1T_1$	22 150	21 800	21 500
$^3T_1$	14 500	14 200	13 700
Dq	2 580	2 560	2 540
B		525	512
C	3 750	3 800	3 900

* Poorly defined shoulder.

Cobalt(II) *Spectra.*—The bands observed for these complexes are recorded below with probable band assignments (units are cm^{-1}):

Excited state and l.f. parameters	$[Co(bipy)_3]^{2+}$	$[Co(amp)_3]^{2+}$	$[Co(en)_3]^{2+}$
$^4T_2$	11 300	10 400	9 800
$^4T_1(P)$	22 000	21 200	
		16 850	
Dq	1 265	1 220	1 180
B	790	800	

Iron(II) *Spectra.*—Here only the spectrum of the amp complex was recorded. A single l.f. band at 12 250 cm^{-1} was observed, which is assigned as $^5T_{2g} \rightarrow {}^5E_g$, so that *Dq* is 1 225 cm^{-1}.



Ultraviolet–visible spectra of $[Ni(bipy)_3]^{2+}$ (——), $[Ni(amp)_3]^{2+}$ (— — —), and $[Ni(en)_3]^{2+}$ (· · · ·)

Nickel(II) *Spectra.*—The spectra of the bipy, amp, and en complexes are shown in the Figure. Band positions for these and the other complexes studied are shown below (units are cm^{-1}):

Excited state and l.f. parameters	$[Ni(bipy)_3]^{2+}$	$[Ni(amp)_3]^{2+}$	$[Ni(en)_3]^{2+}$
$^3T_1(P)$			29 100
$^3T_1(F)$	19 200	18 800	18 400
^1E }	{12 700	12 700	12 700
$^3T_2$ }	{11 600	11 300	11 000
Dq	(1 160)	(1 130)	1 100
B			930
	$[Ni(GlyO)_3]^-$	$[Ni(O_4C_2)_3]^{4-}$	$[Ni(pyca)_3]^-$
$^3T_1(P)$	27 500	25 900	27 750
$^3T_1(F)$	16 650	15 500	17 100
^1E	13 100	13 500	13 100
$^3T_2$	10 000	8 900	10 300
Dq	1 000	890	1 030
B	925	935	915

DISCUSSION

For the amp complexes of Co^{III} and Co^{II}, *Dq* is approximately the average of the *Dq* values of the bipy and en complexes, which suggests that electronic delocalization over the chelate ring plays at most only a small part in producing the high values of *Dq* for the bipy complexes. The chelate-effect model [1] discussed above

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[6] C. L. Rollinson and J. C. Bailar, *Inorg. Synth.*, 1946, **2**, 198.

suggests that where a ligand such as glycinate (GlyO) can be considered to be composed of the halves of two other ligands, in this case $[C_2O_4]^{2-}$ and en, log K_1(GlyO) should be the mean of log $K_1(C_2O_4{}^{2-})$ and log K_1(en). This is true for example for Cu^{II} [log K_1(GlyO) 8.4, log $K_1(C_2O_4{}^{2-})$ 6.2, and log K_1(en) 10.5] or Zn^{II} [log K_1(GlyO) 5.3, log $K_1(C_2O_4{}^{2-})$ 4.8, and log K_1(en) 5.7]. If the failure of equation (2) is due to electronic delocalization over the chelate ring, we would expect the stability of amp complexes, in which such delocalization cannot occur, to be considerably less than the mean of log K_1 for bipy and en. However, as seen below, log K_1(amp) is very nearly the mean of log K_1(bipy) and log K_1(en):

	log K_1					
Ligand	Cu^{II}	Ni^{II}	Co^{II}	Fe^{II}	Zn^{II}	Cd^{II}
en	10.5	7.4	5.7	4.0	5.7	5.4
bipy	8.0	7.1	5.7	4.2	5.0	4.3
amp (calc.)	9.3	7.3	5.7	4.1	5.4	4.9
(obs.)	9.5	7.2	5.5	3.8	5.3	4.7

The l.f. spectra combined with the above formation-constant relations suggest that the high Dq values and formation constants associated with bipy complexes are not dependent on electronic delocalization over the chelate ring. The same conclusion can be drawn from Dq values of the pyca complexes of Ni^{II}, and also from inspection of log K_1 for analogous pyca, $[C_2O_4]^{2-}$, and bipy complexes. The extra stability of complexes of ligands incorporating a pyridyl group in a chelate ring is obviously related to some property of the chelate ring. This might, for example, be the ability of chelating ligands containing the pyridyl group to lie more nearly in the co-ordination plane of the metal ion, thereby promoting π bonding, which is not possible with py since the *o*-hydrogens are sterically hindered by neighbouring ligand molecules when placed in the co-ordination plane. Further work is obviously necessary to test this, and other, suggestions which can be made to explain the extra stability of pyridyl-containing chelate-ligand complexes.

Nickel(II) *L.F. Spectra*.—The band $^3A_{2g}\rightarrow{}^3T_{1g}$ in the l.f. spectrum of $[Ni(amp)_3]^{2+}$ is intermediate in energy compared with the same band of the bipy and en complexes of Ni^{II}, and is therefore similar in behaviour to the bands of the cobalt(II) and cobalt(III) analogues. For the two bands which occur in the 11 000—13 000 cm^{-1} region in the spectra of the en, amp, and bipy complexes of Ni^{II} the position is somewhat more complicated. As pointed out by Jørgensen,[7] this area of the spectrum corresponds to the energetic crossover point of the $^3T_{2g}$ and ^1E_g energy levels. These energy levels cannot actually coincide, and have a minimum separation of $2k$ where k is the energy of the interacting off-diagonal elements. At the same time, the spin-forbidden transition to the ^1E_g level will ' borrow ' intensity from the spin-allowed transition to the $^3T_{2g}$ level.

The two energy levels are actually mixed, and neither of the two peaks can be said to correspond to a pure transition to either of the two energy levels. This has been overlooked by workers who have calculated l.f. parameters, and drawn other conclusions, from the positions of peaks in the spectra of nickel(II) complexes with ^1E_g and $^3T_{2g}$ energy levels in the crossover region. Thus, the band at 12 700 cm^{-1} in the spectrum of $[Ni(bipy)_3]^{2+}$ has been assigned[8] as $^3A_{2g}\rightarrow{}^3T_{2g}$. This assignment leads to an anomalously high value of Dq and a low value of B for this complex. In a series of α-di-imine complexes with N-alkyl substituents of progressively increasing size and hence ability to hinder sterically the formation of the complexes, the ^1E_g level was observed[9] to pass through the $^3T_{2g}$ level, but again mixing of states was not considered in calculating Dq values. From the closest approach of these two bands in the latter study, one concludes that k has a value of *ca*. 440 cm^{-1}. For nickel(II) complexes of a sexidentate ligand containing pyridyl and imine groups, the lower-energy band was assigned as $^3A_{2g}\rightarrow{}^3T_{2g}$.[10] It is probable that the $^3A_2\rightarrow{}^3T_2$ character of each band will be related to its oscillator strength. The shapes of the two bands are altered from simple Gaussian as they become steadily more mixed, and it is not certain at this stage what the shapes of these bands should be, so that no band resolution is attempted here. Examination of the Figure shows, however, that the ratio between the intensity of the higher-energy to the lower-energy band appears to form a series bipy > amp > en, so that, whatever the true position of the transition $^3A_{2g}\rightarrow{}^3T_{2g}$, its position in the amp complex will be intermediate between that in the bipy and en complexes. The $[C_2O_4]^{2-}$ and pyca complexes of Ni^{II} have widely separated $^3T_{2g}$ and ^1E_g energy levels, so that relatively pure transitions to these levels are observed. Since the position of $^3A_{2g}\rightarrow{}^3T_{2g}$ in the pyca complex at 10 300 cm^{-1} should be intermediate between that at 8 900 cm^{-1} in the $[C_2O_4]^{2-}$ complex and this transition in the bipy complex, a value for the bipy complex of 11 700 cm^{-1} is suggested. This indicates that the band at 11 600 cm^{-1} in the spectrum of $[Ni(bipy)_3]^{2+}$ probably contains more $^3A_{2g}\rightarrow{}^3T_{2g}$ character than the band at higher energy. Such a reassignment removes the anomalously high Dq and low B values for this complex.

Iron(II) *L.F. Spectra*.—The transition $^5T_{2g}\longrightarrow{}^5E_g$ occurs[3] at 11 400 cm^{-1} in $[Fe(en)_3]^{2+}$, so that Dq must be 1 140 cm^{-1}. Since Dq is 1 225 cm^{-1} for $[Fe(amp)_3]^{2+}$, expected to be intermediate between Dq in the amp and bipy complexes, we estimate a value of Dq of 1 310 cm^{-1} for $[Fe(bipy)_3]^{2+}$. This value of Dq is that appropriate to the hypothetical high-spin $[Fe(bipy)_3]^{2+}$ complex, since spin pairing is likely[3] to increase the value of Dq, and so should be regarded as a lower limit to Dq in $[Fe(bipy)_3]^{2+}$. Large c.t. bands obscure the l.f. spectrum in the latter complex, so that no experimental value of Dq for this complex is available. The intermediacy of

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[7] C. K. Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

[8] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 864.

[9] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, 1963, **2**, 1178.

[10] L. J. Wilson, D. Georges, and M. A. Hoselton, *Inorg. Chem.*, 1975, **14**, 2968.

amp between en and bipy in bonding properties is further illustrated by the fact that $[Fe(bipy)_3]^{2+}$ is spin paired, $[Fe(en)_3]^{2+}$ is spin free, but $[Fe(amp)_3]^{2+}$ shows temperature-dependent magnetic isomerism[11] at low temperatures.

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[6/834 *Received*, 30*th April*, 1976]

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[11] G. A. Renovitch and W. A. Barker, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 6377.