Mononuclear and Polynuclear Complexes of Cobalt(II) Carboxylates with Pyridine and other Heterocyclic Bases

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Adducts of cobalt(II) carboxylates with pyridine and related ligands have been prepared, their electronic spectra assigned, and their magnetic properties investigated. The complex $[Co(py)_2(O_2CPh)_2]$ (py = pyridine) behaves as a six-co-ordinate species whose electronic spectrum shows tetragonal splitting; $[Co(2\text{-}Mepy)(O_2CPh)_2]$ has the properties of a trigonal-bipyramidal five-co-ordinate high-spin complex. The green complexes $[Co_2(quin)_2(O_2CR)_4]$ (R = Ph or $C_6H_4NO_2$-2; quin = quinoline) are antiferromagnetic binuclear species with square-pyramidal five-co-ordination. A slate-blue form of $[Co(quin)(O_2CC_6H_4NO_2\text{-}2)_2]$ behaves as a slightly antiferromagnetic polymer. The complexes $[Co_3(quin)_2(O_2CR)_6]$ (R = Ph or $C_6H_4NO_2$-2) contain a linear array of two trigonal-bipyramidal and one octahedral cobalt atoms and are not appreciably antiferromagnetic.

THE most deeply studied[1,2] group of polynuclear co-ordination compounds is $[Cu_2(OH_2)_2(O_2CMe_2)_4]$ and other binuclear copper(II) carboxylates, so that there is now a large body of information about complexes which contain two spins of $\frac{1}{2}$. We have now studied the reactions of some cobalt(II) carboxylates with heterocyclic amines in order to extend the range of metal ions for which dimeric or other cluster carboxylates can be prepared. Preliminary communications on this aspect of our work have already been published.[3,4]

Although the assignment of the electronic spectra of the 3*d* elements is often easy, those of high-spin cobalt(II) complexes are unusually difficult to analyse.[5] In octahedral complexes three spin-allowed *d–d* transitions are expected from $^4T_{1g}(F)$ to $^4T_{2g}$ (ν_1), $^4A_{2g}$ (ν_2), and $^4T_{1g}(P)$ (ν_3). These three bands differ markedly in appearance. The first band is often broad and ν_3 is usually the strongest, but ν_2, the 'two-electron' transition, is hard to identify and often appears as a shoulder on the much stronger ν_3. Both ν_1 and ν_3 are often split, possibly by spin–orbit coupling, although this has been doubted,[6] by transitions to doublet states and by tetragonal distortions.

There have been a number of reports of splittings in the electronic spectra of *cis*-disubstituted pseudo-octahedral cobalt(II) complexes. These involve the chelating anions nitrate[7–9] or nitrite.[10] Studies of *trans*-disubstituted complexes are rarer. Adducts of 2,2′-diaminobiphenyl with cobalt(II) halides and thiocyanate show [11] tetragonal effects clearly as the symmetry round Co^{2+} falls from O_h to D_{4h} and D_{2h}. Lever and Ogden found[6] that tetragonal distortions were less obvious in the pyridine complexes of $[Co(O_2CCH_nX_{(3-n)})_2]$ (X is Cl or F), and a transition to a component of the ^2G free-ion term was considered to contribute to the splitting of ν_3. We have already reported[12] studies of the electronic spectra of related nickel(II) complexes.

RESULTS AND DISCUSSION

Preparation of Complexes.—The complexes were prepared by treating an ethanolic solution of $[Co(O_2CPh)_2]$ or solid $[Co(OH_2)_2(O_2CC_6H_4NO_2\text{–}2)_2]$ with an excess of the heterocyclic base. Usually only one complex resulted but two products were formed between quinoline (quin) and $[Co(O_2CPh)_2]$ and three between quin and $[Co(O_2CC_6H_4NO_2\text{–}2)_2]$. Schemes 1 and 2 describe these systems.

$[Co(py)_2(O_2CPh)_2]$.—Although cobalt(II) halogeno-

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[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[2] R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J.C.S. Dalton*, 1972, 428 and 136 refs. therein.

[3] J. Drew, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J.C.S. Chem. Comm.*, 1973, 52.

[4] J. Catterick, M. B. Hursthouse, D. B. New, and P. Thornton, *J.C.S. Chem. Comm.*, 1974, 843.

[5] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, 1968.

[6] A. B. P. Lever and D. Ogden, *J. Chem. Soc.* (*A*), 1967, 2041.

[7] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 1963, **2**, 1162.

[8] A. B. P. Lever, *Inorg. Chem.*, 1965, **4**, 1042.

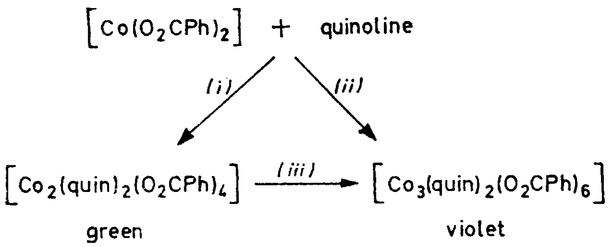
[9] H. N. Ramaswamy and H. B. Jonassen, *Inorg. Chem.*, 1965, **4**, 1595.

[10] L. El-Sayed and R. O. Ragsdale, *Inorg. Chem.*, 1967, **6**, 1644.

[11] B. J. A. Kakazai and G. A. Melson, *Inorg. Chim. Acta*, 1970, **4**, 360.

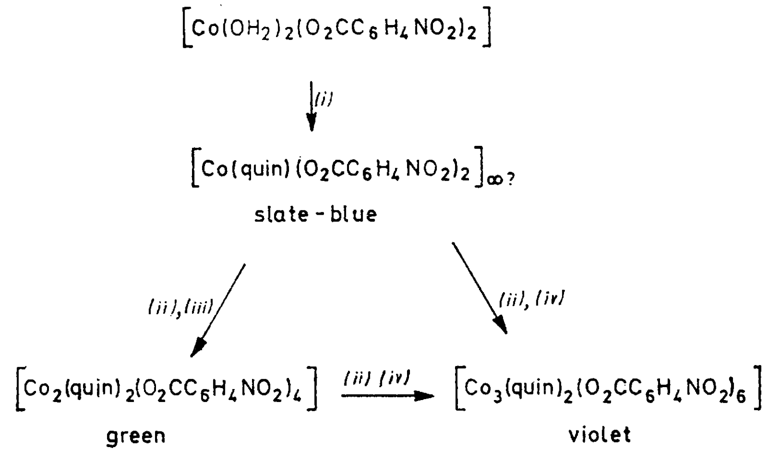
[12] J. Catterick and P. Thornton, *J.C.S. Dalton*, 1975, 233.

carboxylates form adducts containing four or two molecules of pyridine,[6] we were able to prepare only one 2 : 1 complex with the cobalt(II) arylcarboxylates; the other preparations gave 1 : 1 or 2 : 3 ratios of ligand to metal.



SCHEME 1 (*i*) Hot; (*ii*) cold; (*iii*) recrystallise, EtOH

The magnetic moment of 4.78 B.M.* shown by [Co(py)$_2$(O$_2$CPh)$_2$] at 298 K, and its temperature variation (Table 1), show the complex to be slightly less paramagnetic than most octahedral high-spin cobalt(II) complexes, but the Weiss constant of 14 K is normal and does not indicate any significant antiferromagnetism.[13]



SCHEME 2 (*i*) quin; (*ii*) CHCl$_3$; (*iii*) cold; (*iv*) hot

TABLE 1

Magnetic susceptibilities (c.g.s.units) and moments (B.M.)

	[Co(py)$_2$(O$_2$CPh)$_2$]		[Co(2-Mepy)(O$_2$CPh)$_2$]		[Co(quin)(O$_2$CC$_6$H$_4$NO$_2$)$_2$] (green)	
T/K	$10^3\chi_M$	μ	$10^3\chi_M$	μ	$10^3\chi_M$	μ
298	9.61	4.78	10.63	5.03	7.13	4.12
273	10.34	4.75	11.46	5.00	7.44	4.02
223	12.51	4.72	14.05	5.00	7.87	3.74
173	15.98	4.70	17.62	4.94	8.20	3.37
123	21.9	4.64	23.8	4.83	7.86	2.78
98	26.4	4.55	28.8	4.75	7.35	2.40
	[Co(quin)(O$_2$CC$_6$H$_4$NO$_2$)$_2$] (blue)		[Co$_3$(quin)$_2$(O$_2$CPh)$_6$]		[Co$_3$(quin)$_2$(O$_2$CC$_6$H$_4$NO$_2$)$_6$]	
298	7.54	4.23	9.96	4.87	9.67	4.80
273	8.13	4.31	10.74	4.84	10.40	4.77
223	9.63	4.14	13.04	4.82	12.68	4.75
173	11.72	4.03	16.32	4.75	16.03	4.71
123	14.55	3.78	22.1	4.67	21.1	4.56
98	16.28	3.57	26.8	4.58	25.6	4.48

The rather low values for the magnetic moment probably mean that the inequivalence of the pyridine and benzoate ligands causes the $^4T_{2g}$ ground state of an octahedral structure to split to give an orbital-singlet ground state. Similarly, low magnetic moments have been found for a number of other six-co-ordinate high-spin cobalt(II) complexes.[7-10,14,15]

The diffuse-reflectance electronic spectrum of [Co(py)$_2$(O$_2$CPh)$_2$] is shown in Figure 1. At room temperature ν_1 is split into two components, at 7 600 and 9 800 cm^{-1}. This compares reasonably with transitions at 7 500 and 8 800 cm^{-1} in [Co(2-Mepy)$_2$(NO$_3$)$_2$] in which the somewhat lower splitting may be due to a *cis* configuration,[8] with our complex possibly having the *trans* configuration. The strong band at 19 500 cm^{-1} can confidently be assigned to ν_3, which suggests that the shoulder at 17 000 cm^{-1} is the weak ν_2 transition.

As a test of the assignments of ν_2, Lever and Ogden[6] suggest that ν_2/ν_1 should lie between 2.1 and 2.2. In practice this quantity tends to be slightly lower, being 2.02 for CoCl$_2$,[16] 2.12 for KCoF$_3$,[16] and 2.94 for [Co(py)$_2$(O$_2$CCHCl$_2$)].[6] For [Co(py)$_2$(O$_2$CPh)$_2$] ν_2/ν_1 is 2.12. Although the rule only applies for regular octahedral

* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[13] P. W. Ball and A. B. Blake, *J.C.S. Dalton*, 1974, 852.

[14] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

[15] M. N. Hughes and K. J. Rutt, *J. Chem. Soc.* (*A*), 1968, 2788.

[16] J. Ferguson, D. Wood, and K. Knox, *J. Chem. Phys.*, 1963, **39**, 881.

complexes, small deviations should not make much difference, but ν_1 will be more affected as it is a transition between two orbital-triplet states. An alternative criterion involves applying equations proposed by König[17] for calculating average Dq and B values from observed positions of ν_1 and ν_3 and using these to calculate ν_2. This calculation leads to ν_2 appearing at 18 000 cm^{-1} for our complex, slightly higher than the observed shoulder, but this method also does not allow for low-symmetry effects. Contributions from components of the free-ion ^2G or ^2H terms could give structure to ν_3 as could low-symmetry splitting of the orbital-triplet ground and excited states.

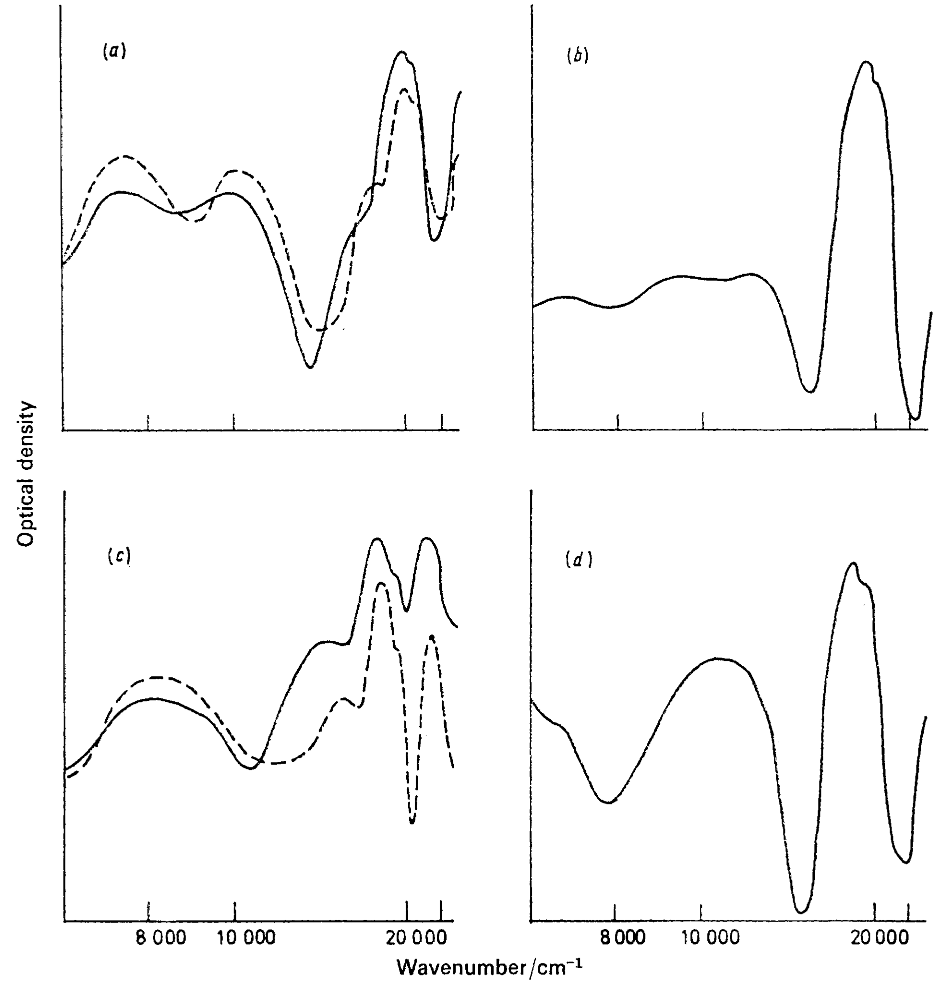


FIGURE 1 Diffuse-reflectance spectra: (a) [Co(py)$_2$(O$_2$CPh)$_2$]; (b) [Co(2-Mepy)(O$_2$CPh)$_2$]; (c) [Co$_2$(quin)$_2$(O$_2$CPh)$_4$]; (d) [Co$_3$(quin)$_2$(O$_2$CPh)$_6$]; (——) spectra at room temperature; (— — —) spectra at low temperature

Figure 1 also shows the low-temperature reflectance spectrum, the chief development being the clarification of the proposed ν_2 and its shift to *ca.* 17 000 cm^{-1}. This agrees with the assignment since in the Tanabe–Sugano diagram the gradient dE/dΔ is steep for the A_{2g} state.

Confirmation of electronic-spectral assignments in distorted octahedral cobalt(II) complexes requires the use of single-crystal polarised spectra[18-20] or magnetic circular dichroism studies.[21] As the complex is not crystalline we cannot speculate further on its spectrum. It is only soluble in chloroform, but the solution changes from the pale pink colour of the complex to a bright purple, with the formation of a pale pink suspension, possibly of [Co(O$_2$CPh)$_2$]. This decomposition occurs even when pyridine is added to the solution.

Although the physical properties of [Co(py)$_2$(O$_2$CPh)$_2$] indicate an octahedral environment for Co^{2+} we cannot tell whether the complex is monomeric with chelating benzoate groups or a dimer or other polymer with bridging benzoates as well. For the corresponding halogenocarboxylates[6] an attempt was made to distinguish these possibilities by i.r. spectra taken in the solid state and in solution in chloroform. In solution these

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[17] E. König, *Z. Naturforsch.*, 1972, **B27**, 1.

[18] P. D. Hu and A. L. Companion, *Phys. Status Solidi*, 1973, **B56**, 261.

[19] J. Ferguson, T. E. Wood, and H. J. Guggenheim, *Inorg. Chem.*, 1975, **14**, 177.

[20] J. Ferguson and T. E. Wood, *Inorg. Chem.*, 1975, **14**, 184, 190.

[21] T. E. Kaden, B. Holmquist, and B. L. Vallee, *Inorg. Chem.*, 1974, **13**, 2585.

complexes showed two antisymmetric CO_2 stretching frequencies, one being more intense in dilute solution but absent from the solid-state spectrum. It was concluded that the dilute solution contained monomers and the concentrated solutions and solid state contained dimers, but there was no consideration of the likely loss of pyridine from the complexes in solution.

$[Co(2\text{-}Mepy)(O_2CPh)_2]$.—The complexes having the stoicheiometry $CoL(O_2CR)_2$ fall into three types: magnetically normal, strongly antiferromagnetic, and weakly antiferromagnetic.

The complex $[Co(2\text{-}Mepy)(O_2CPh)_2]$ has a room-temperature moment of 5.03 B.M., decreasing slightly at lower temperatures (Table 1). The data follow a Curie–Weiss law with a small Weiss constant of 19°, typical of a magnetically isolated Co^{2+} ion in an orbitally degenerate ground state.[13] Again, the i.r. spectra do not give a clear indication of geometry, but the identification[22] of chelating benzoate groups in monomeric $[Ni(2\text{-}Mepy)_2(O_2CPh)_2]$ suggests there is no impediment to forming a five-co-ordinate structure for the cobalt complex. There is no clear trend in the magnetic behaviour of high-spin five-co-ordinate cobalt(II) complexes, with room-temperature values of the magnetic moment ranging from 4.45 B.M. for $[CoCl(Me_3tren)]Cl$ [ref. 23; $Me_3tren = N(CH_2CH_2NHMe)_3$] to 5.5 B.M. for square-pyramidal[24] $[Co(AsMePh_2O)_4(ClO_4)][ClO_4]$. One of the more important variables in this problem is the deviation of bond angles from regularity,[25] which makes rationalisation difficult when molecular dimensions are unknown. The earlier results closest to our data are those[26] for $[CoCl_2(terpy)]$ (terpy = 2,2′ : 6′,2″-terpyridyl) whose magnetic moment is 5.03 B.M. at 291.5 K and 4.89 B.M. at 94 K.

The diffuse-reflectance spectrum (Figure 1) showed maxima at 7 250, 9 200, 11 400, and 18 200 cm^{-1}, but has no close parallel with other five-co-ordinate cobalt(II) complexes, which themselves show considerable variation. This is probably partly due to the fact that none of the previously studied complexes contained the $CoNO_4$ chromophore present here, and partly due to the appreciable deviations from regular symmetry which occur in most of the complexes. Despite the difficulty of assignment, we believe the complex has approximately trigonal-bipyramidal geometry as its spectrum is unlike that of $[Co_2(quin)_2(O_2CPh)_4]$ which has been found crystallographically[3] to have square-pyramidal co-ordination and is discussed in the next section.

The splitting of the ^4F and ^4P free-ion terms in weak-field D_{3h} symmetry is shown[5] in Figure 2(*a*). Transitions should be observed to all five excited states. We assign the first three weaker bands to the transitions to components of ^4F and the strong band at 18 200 cm^{-1} to a component of ^4P in line with a recent report and assignment[27] of the spectrum of $[Co(2\text{-}Mepyo)_5]^{2+}$ (2-Mepyo = 2-methylpyridine *N*-oxide). If this is $^4E''$ (*P*) a transition to $^4A_2'$ (*P*) would be expected near 15 000—16 000 cm^{-1}, but this is not seen, whereas if it is to the $^4A_2'$ state then the transition to $^4E''$ is missing. However, the strong band is unsymmetrical and the inevitable deviation from D_{3h} to C_{3v} or C_{2v} symmetry will cause some adjustment of the energy levels.[27] Transitions to derivatives of the ^2G free-ion term probably also contribute to the multiplet structure of this band.

In the absence of *X*-ray data on the non-crystalline complex it is unwise to speculate on whether the trigonal-bipyramidal cobalt atom has the 2-Mepy group at the axial or equatorial position, but there would be less distortion from regularity if the chelating benzoate groups each occupy one axial and one equatorial site, leaving the third equatorial site for the 2-Mepy ligand.

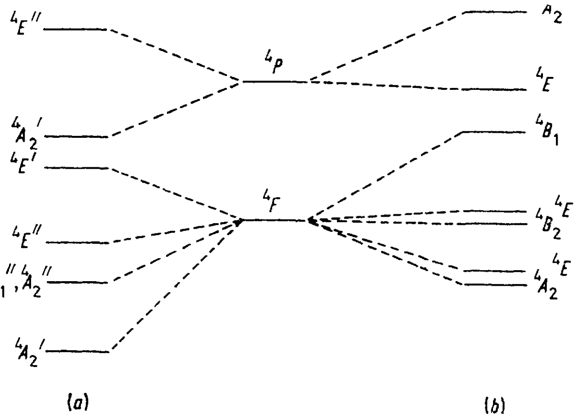

FIGURE 2 Splitting of Co^{2+} free-ion levels in D_{3h} (*a*) and in C_{4v} symmetry (*b*)

$[Co_2(quin)_2(O_2CPh)_4]$ *and* $[Co(quin)(O_2CC_6H_4NO_2\text{-}2)_2]$ (*Green Isomer*).—Quinoline is the only ligand to form more than one polynuclear complex with a cobalt(II) carboxylate. As Schemes 1 and 2 show, both cobalt(II) benzoate and 2-nitrobenzoate form green complexes of stoicheiometry $Co(quin)(O_2CR_2)_2$, and for the nitrobenzoate a slate-blue isomer is also produced. This shows some differences from the green complexes and will be discussed separately.

An *X*-ray structural analysis[3] of the benzoate complex showed it to have dimeric structure (I) analogous to that[1,2] of $[Cu_2(OH_2)_2(O_2CMe)_4]$ and many other complexed copper carboxylates. The molecule has a cobalt–cobalt separation of 2.832 Å and some steric interactions which result in unequal Co–O distances and N–Co–O angles. The cobalt atoms have approximately square-pyramidal five-co-ordination.

Both complexes exhibit antiferromagnetism in common with the many copper(II) carboxylates with this type of structure. For the benzoate the magnetic moment decreases from 4.41 B.M. at 373 K to 1.71 B.M.

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[22] D. B. New, Ph.D. Thesis, London, 1975.

[23] M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.

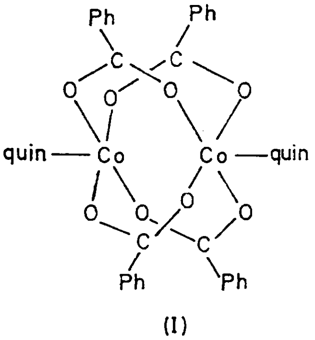
[24] J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, 1965, **207**, 72.

[25] J. S. Wood, *Progr. Inorg. Chem.*, 1972, **16**, 227.

[26] F. Lions, I. G. Dance, and J. Lewis, *J. Chem. Soc.* (*A*), 1967, 565.

[27] I. Bertini, P. Dapporto, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, 1975, **14**, 1639.

at 98 K, with a maximum in susceptibility at 268 K. The magnetic moment of the nitrobenzoate complex decreases from 4.12 B.M. at 298 K to 2.40 B.M. at 98 K, with a maximum in susceptibility at 173 K, so this complex appears also to be dimeric, with the small differences in magnetic behaviour probably resulting from small differences in bond lengths and angles in the bridging groups. The theoretical treatment [28] of antiferromagnetic interactions involving orbitally degenerate ground states is much more complex than the simple method [29] appropriate for copper(II) dimers and its application will be described elsewhere.[30]



(I)

TABLE 2

Electronic spectra (cm^{-1}) of complexes with C_{4v} symmetry

	ν_1		ν_2		ν_3 [a]		ν_4	
	R.t.[b]	L.t.[c]	R.t.	L.t.	R.t.	L.t.	R.t.	L.t.
[$Co_2(quin)_2(O_2CPh)_4$]	8 100	8 100	13 500	14 600	17 400 (18 900)	17 400 (18 900)	22 500	22 800
[$Co(quin)(O_2CC_6H_4NO_2)_2$] (green)	8 100	8 100	13 200	13 700	17 100 (18 800)	17 100 (18 800)	21 600	21 900
[$Co(quin)(O_2CC_6H_4NO_2)_2$] (blue)	7 700	7 700	12 800	13 100	17 100	17 100	21 300	21 400
Calc. (ref. 33)	7 600		14 100		17 100		22 300	

[a] Shoulders are given in parentheses. [b] R.t. = Sample at room temperature. [c] L.t. = Sample cooled by liquid nitrogen.

The electronic spectra of both complexes are similar. The band maxima are listed in Table 2 and the spectrum of the benzoate at room temperature and when cooled by liquid nitrogen is shown in Figure 1. The spectra can be treated on the basis of a square-pyramidal $CoNO_4$ chromophore, and there is no need to invoke the participation of low-energy charge-transfer transitions like those needed to explain [31,32] completely the spectra of dimeric copper(II) carboxylates.

The energy-level diagram [33] for high-spin square-pyramidal Co^{II} is shown in Figure 2(*b*). This has used a value of 100° for the vertical angle α at the metal atom (the mean of the experimentally determined angles for the benzoate is 98.2°). The lowest ^4E excited state is at too low an energy for its transition to be detected, and transitions to the $^4B_2$ level are ' two-electron jumps ' in the strong-field limit, so that the four observed bands can be assigned to transitions to $^4E(F)$, $^4B_1$, $^4E(P)$, and $^4A_2$. Table 2 also shows the calculated energies from Ciampolini and Bertini's energy-level diagram [33] with a *Dq* of 900 cm^{-1}. The minor deviations can be attributed to deviations from regular C_{4v} symmetry. The assignments are favoured by the shifts of bands on cooling. Most of the shifts are very small, the greatest change being in the transition to $^4B_1$ which increases by 1100 cm^{-1} for the benzoate complex and 500 cm^{-1} for the nitrobenzoate. This band is expected to be the most susceptible to temperature variation because the energy separation between $^4B_1$ and the $^4A_2(F)$ ground state varies more with *Dq* than any other separation. The unassigned shoulder at 18 800—18 900 cm^{-1} may be a transition to a component of the ^2G free-ion term. The spectra are similar to that [24] of [$Co(AsMePh_2O)_4(ClO_4)$][ClO_4], in which α has been found [34] to be 100°.

[$Co(quin)(O_2CC_6H_4NO_2\text{-}2)_2$] (*Blue Isomer*).—The slate-blue isomer of [$Co(quin)(O_2CC_6H_4NO_2\text{-}2)_2$] (Scheme 2) is not as antiferromagnetic as the green, presumably dimeric, form (Table 1). There is no maximum in the susceptibility above 98 K but the values of magnetic moment and the Weiss constant of 38 K show that the complex is not magnetically dilute.

Two isomers have been recorded [35,36] for dimeric [$Cu_2(py)_2(O_2CMe)_4$], differing only in the orientation of the pyridine groups, but this does not produce such a difference in magnetic properties as that encountered here. Isomerism could also arise from the disposition of the nitro-substituents, with probable steric hindrance causing variations in the Co–O–C–O–Co superexchange path length, but our difference in magnetic properties is greater than any occurring in the many variations of ligands and anions found in dimeric copper(II) carboxylates. We suspect that the slate-blue isomer is not a dimer but a polymer. The 4-toluidine adduct of copper(II) propionate has a complex polynuclear structure [37] with pairs of copper atoms linked by only two carboxylate bridges, and this complex shows antiferromagnetism

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[28] M. E. Lines, *J. Chem. Phys.*, 1971, **55**, 2977.

[29] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, 1952, **A214**, 451.

[30] J. Catterick, K. D. Sales, and P. Thornton, unpublished work.

[31] L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 2203.

[32] L. Dubicki, *Austral. J. Chem.*, 1972, **25**, 1141.

[33] M. Ciampolini and I. Bertini, *J. Chem. Soc.* (*A*), 1968, 2241.

[34] P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, 1965, **207**, 73.

[35] G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 5244.

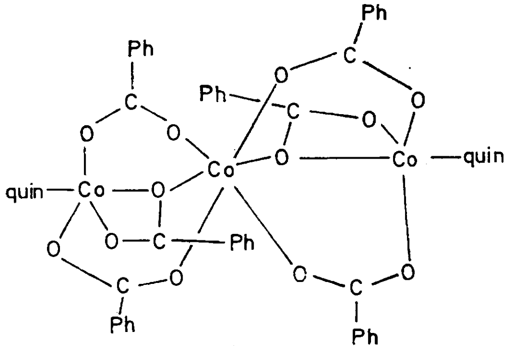
[36] F. Hanic, D. Stempelova, and K. Hanicova, *Acta Cryst.*, 1964, **17**, 633.

[37] D. B. W. Yawney, J. A. Moreland, and R. J. Doedens, *J. Amer. Chem. Soc.*, 1973, **95**, 1164.

which is less marked than that of the copper(II) dimers, so the behaviour of our complex is consistent with a polymeric structure of this type.

The structure of this isomer must include an approximately square-pyramidal $CoNO_4$ chromophore since the electronic spectrum is very similar to that of the green dimers (Table 2). The difference in colour arises from small variations in the energies of the transitions, which occur at an average of 300 cm^{-1} to lower energy in the blue than in the green forms.

$[Co_3(quin)_2(O_2CR)_6]$.—This pair of complexes has been found (Schemes 1 and 2) for R = Ph and $C_6H_4NO_2$-2. The structures have been determined[4,22] by *X*-ray crystallography to be linear trinuclear molecules (II).



(II)

Each pair of cobalt atoms is bridged by three carboxylate groups, but some twisting of the bridging groups results in two oxygen atoms being co-ordinated to two cobalt atoms. The quinoline groups are co-ordinated to the terminal cobalt atoms, giving one octahedral cobalt atom and two trigonal-bipyramidal ones. The cobalt–cobalt separation is 3.559 Å in the benzoate and 3.552 Å in the nitrobenzoate, much longer distances than that of 2.832 Å in dimeric $[Co_2(quin)_2(O_2CPh)_4]$. In both complexes the NCoO angles have a mean value of 100°, as found in the dimer, so that the trigonal bipyramid is not regular, but the co-ordination round the central cobalt atom is regularly octahedral.

Above 98 K the magnetic properties of these complexes are those of magnetically isolated Co^{2+} ions (Table 1). The values are consistent with averaging the usual results for two orbitally non-degenerate and one orbitally degenerate high-spin Co^{2+}. Both complexes follow the Curie–Weiss law, with small θ values of 20° for the benzoate and 22° for the nitrobenzoate. These results are surprising as carboxylate-bridged metal ions usually show antiferromagnetic interactions and this effect is particularly strong in the $[Co_2(quin)_2(O_2CR)_4]$ complexes. The magnetic interactions in the trimers will be particularly complex since the cobalt atoms are inequivalent and the carboxylates form triatomic and monatomic bridges. There are bound to be ferromagnetic and antiferromagnetic contributions to the exchange and the measurements suggest these approximately cancel one another in the trimers but that antiferromagnetic coupling predominates in the dimers.

The electronic spectra of the trinuclear complexes would be expected to resemble that of a similar trigonal-bipyramidal complex. The spectrum of the benzoate is shown in Figure 1 where the resemblance to the spectrum of $[Co(2\text{-}Mepy)(O_2CPh)_2]$ is clear, and supports our conclusion that this has a trigonal-pyramidal configuration although there are some differences in relative intensities. For the benzoate, absorptions occur at 7 100 (sh), 10 600, 18 100, and 19 200 cm^{-1} (sh); for the nitrobenzoate, the maxima are at 7 100 (sh), 10 800, 17 700, and 19 200 cm^{-1} (sh).

EXPERIMENTAL

Analysis.—Cobalt was determined with a Perkin-Elmer 303 atomic-absorption spectrophotometer, and carbon, hydrogen, and nitrogen by standard microanalysis in the Alfred Bernhardt laboratories, with extra oxidant added to ensure complete combustion.

Instrumentation.—Electronic spectra were recorded on a Beckman DK-2A spectrophotometer with a standard diffuse-reflectance attachment. Our modification for cooling samples has already been described.[12] I.r. spectra were obtained as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 337 spectrophotometer. Magnetic-susceptibility measurements were made by the Gouy method using a Newport variable-temperature balance over the range 98—373 K at three different field strengths, with calibration by $Hg[Co(NCS)_4]$.[38]

Preparations.—*Ethanolic solution of dibenzoatocobalt*(II). Benzoic acid (18.0 g) was dissolved in hot ethanol (250 cm^3). The solution was filtered into basic cobalt(II) carbonate ($2Co[CO_3]\cdot 3Co[OH]_2$, 12.5 g). The resulting solution was heated under reflux for 18 h, yielding a spongey brown precipitate which was removed by three filtrations leaving a mauve ethanolic solution of dibenzoatocobalt(II). Batches of solution thus prepared were used in preparing the benzoato-complexes.

Dibenzoatodipyridinecobalt(II). Pyridine (15 cm^3) was added to an ethanolic solution of $[Co(O_2CPh)_2]$ to give a very dark mauve solution, which was heated under reflux for 30 min. The solution was filtered while hot and precipitated a pale pink solid on cooling. This was recrystallised from ethanol, washed with diethyl ether, and dried over $CaCl_2$ and H_2SO_4 *in vacuo*. The other complexes were dried this way unless otherwise stated, yield 3.0 g [5.4% from basic cobalt(II) carbonate] (Found: C, 62.8; H, 4.50; Co, 12.8; N, 6.00. Calc. for $C_{24}H_{20}CoN_2O_4$: C, 62.75; H, 4.40; Co, 12.85; N, 6.10%).

Dibenzoato(*2-methylpyridine*)*cobalt*(II). 2-Methylpyridine (15 cm^3) was added to an ethanolic solution of $[Co(O_2CPh)_2]$ to give a dark mauve solution, which was filtered and left to crystallise. The violet crystals which were deposited were filtered off, washed with light petroleum (b.p. 40—60 °C), and dried, yield 2.2 g (4.6%) (Found: C, 60.7; H, 4.45; Co, 15.5; N, 3.70. Calc. for $C_{20}H_{17}CoNO_4$: C, 60.9; H, 4.30; Co, 14.95; N, 3.55%).

Tetrabenzoatodiquinolinedicobalt(II). Quinoline (20 cm^3) was added to an ethanolic solution of $[Co(O_2CPh)_2]$ to give a dark red solution. This was heated under reflux for 1 h, filtered while hot, and left to crystallise overnight. The dark green crystals were filtered off, washed with diethyl ether, and dried, yield 2.7 g (5.2%) (Found: C, 64.2;

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[38] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

H, 4.05; Co, 14.3; N, 3.30. Calc. for $C_{23}H_{17}CoNO_4$: C, 64.2; H, 4.00; Co, 13.7; N, 3.25%).

Hexabenzoatodiquinolinetricobalt(II). Quinoline (12.5 cm³) was added to an ethanolic solution of $[Co(O_2CPh)_2]$ to give a dark red solution. This was filtered and left to stand for 3 d. Violet crystals were deposited, filtered off, recrystallised from ethanol, washed with diethyl ether, and dried, yield 1.2 g (2.5%). The complex was also prepared by refluxing $[Co_2(quin)_2(O_2CPh)_4]$ (1.0 g) in ethanol (30 cm³) to give a light pink suspension and a mauve solution, which was filtered while hot. Violet crystals were obtained when the filtrate was cooled, yield 0.45 g {48% based on $[Co_2(quin)_2(O_2CPh)_4]$} (Found: C, 61.7; H, 3.80; Co, 15.1; N, 2.50. Calc. for $C_{60}H_{44}Co_3N_2O_{12}$: C, 62.0; H, 3.80; Co, 15.2; N, 2.40%).

Diaquabis(2-*nitrobenzoato*)*cobalt*(II). 2-Nitrobenzoic acid (25.0 g) was dissolved in hot ethanol (250 cm³) and filtered into basic cobalt(II) carbonate (15.0 g). After refluxing for 18 h the mauve solution was filtered until clear, concentrated under reduced pressure, and left to crystallise. The mauve crystals were recrystallised from ethanol, washed with a little hot ethanol, and dried in an oven at *ca.* 80 °C, yield 5.1 g [8.2% from basic cobalt(II) carbonate] (Found: C, 39.5; H, 2.75; Co, 14.1; N, 6.50. Calc. for $C_{14}H_{12}CoN_2O_{10}$: C, 39.35; H, 2.85; Co, 13.8; N, 6.55%).

Bis(2-*nitrobenzoato*)*quinolinecobalt*(II) (*blue isomer*). Diaquabis(2-nitrobenzoato)cobalt(II) (3.6 g) was dissolved in quinoline (25 cm³) and heated under reflux for 3 h. On standing for 2 d, dark slate-blue crystals were formed. These were filtered off, washed with diethyl ether, and dried, yield 2.3 g {52% based on $[Co(OH_2)_2(O_2CC_6H_4NO_2)_2]$} (Found: C, 53.1; H, 3.00; Co, 11.7; N, 7.90. Calc. for $C_{23}H_{15}CoN_3O_8$: C, 52.95; H, 2.90; Co, 11.3; N, 8.05%).

Bis(2-*nitrobenzoato*)*quinolinecobalt*(II) (*green isomer*). When the slate-blue complex was added to chloroform the green isomer was formed in almost quantitative yield (Found: C, 52.9; H, 3.00; Co, 11.3; N, 8.10%).

Hexa(2-*nitrobenzoato*)*diquinolinetricobalt*(II). Either form of $[Co(quin)(O_2CC_6H_4NO_2\text{-}2)_2]$ (2.0 g) was heated under reflux in chloroform for 1 h to yield bright violet crystals which were filtered off, washed with diethyl ether, and dried, yield 1.4 g {80% based on $[Co(quin)(O_2CC_6H_4NO_2)_2]$} (Found: C, 50.2; H, 2.70; Co, 12.0; N, 7.70. Calc. for $C_{60}H_{38}Co_3N_8O_{24}$: C, 50.3; H, 2.70; Co, 12.35; N, 7.80%).

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