the bound acetonitrile was recorded as a function of time. Areas under the peaks were checked by curve-fitting techniques using a du Pont 310 spectrum analyzer. The $t_\infty$ integral was subtracted from all previous time integrals, and the logarithms of these corrected values were plotted vs. time. These data were subjected to a linear least-squares analysis performed by conventional computer techniques.

**Crown Ether Assisted Aquation of Nitrobis(ethylenediamine)-acetonitrilocobalt(III).** To 0.0375 g of $[Co(en)_2(CH_3CN)_2(NO_2)](ClO_4)_2$ was added 1.0 mL of a $D_2O$ solution, originally buffered at pD 4.4 with potassium hydrogen phthalate,[14] containing various concentrations of 18-crown-6. The crown ether concentrations used were in 3.5–10-fold excess over that of the cobalt complex. Temperatures were controlled and the kinetics of aquation were monitored in the same manner as outlined in the previous section. 15-Crown-5, purchased from the Parish Chemical Co., was used in a similar manner to that of 18-crown-6.

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(14) An observed pD independence of the aquation of **2** negated the necessity of adding KHP. When KHP was used, the crown ether assisted kinetics showed no rate enhancement in the aquation of **2** by crown ethers. This was presumably a result of the formation of a potassium–crown complex.

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Contribution from the Laboratorio CNR and the Istituto di Chimica Generale, University of Florence, Florence, Italy

# Single-Crystal Polarized Electronic Spectra of the Dimeric Tetrakis($\mu$-benzoato-*O*,*O*′)-bis(quinoline)dicobalt(II)

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The electronic spectra of copper(II) carboxylate dimers have been interpreted in several different ways according to the model chosen to describe the magnetic coupling in the dimeric units.[1-8] However, in the last few years it has become widely accepted that the direct metal–metal interaction must be considered as a small perturbation on the tetragonal ligand field and that the magnetic coupling is mainly due to superexchange effects. In this framework the band at ≃700 nm was attributed to the d–d transitions, while the band at ≃370 nm was attributed to a ligand-to-metal charge transfer. The best support to this assignment is given by the paper by Dubicki,[8] reporting single-crystal spectra in the range 4.2–290 K.

The X-ray crystal structure determination of tetrakis($\mu$-benzoato-*O*,*O*′)-bis(quinoline)dicobalt(II), $Co_2(bz)_4(quin)_2$, has shown that the complex is structurally quite similar to copper acetate monohydrate.[9] The magnetic moment ranging from 4.4 $\mu_B$ at room temperature to 1.72 $\mu_B$ at liquid nitrogen temperature[10] shows that antiferromagnetic coupling is operative, although no value for *J* could be calculated due to the complicated nature of the ground levels. It appeared to us quite interesting to study the single-crystal polarized electronic spectra of this compound, since no other cobalt(II) dimeric complex of this type has been reported up to now.[11] The electronic spectra of cobalt(II) complexes show in general several bands, which are narrower than those of copper(II) complexes where often only one broad featureless band is the envelope of all the d–d transitions. Therefore a detailed analysis of the electronic spectra of dimeric cobalt(II) complexes might in principle offer more information on the electronic levels in dimers than can be provided by copper(II) spectra. We wish now to report the single-crystal polarized electronic spectra of $Co_2(bz)_4(quin)_2$ in the range 4.2–290 K.

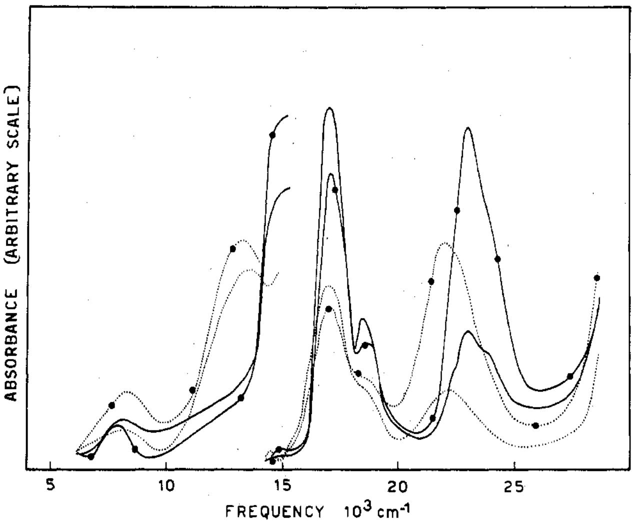

**Figure 1.** Single-crystal polarized electronic spectra of the $Co_2(bz)_4(quin)_2$ complex recorded at 290 K (···) and 4.2 K (—) on the (010) face. The traces with ● are the spectra recorded with the electric vector parallel to *a*; the others have the electric vector parallel to *c*.

## Experimental Section

The compound was obtained by addition of a large excess of quinoline to a boiling solution of benzoic acid and $Co(BF_4)_2 \cdot 6H_2O$ in butanol. After 3 days, deep green crystals were collected and washed with ethanol and petroleum ether. The crystals were found by Weissenberg techniques to correspond to the structure report,[9] with the (010) face most developed.

Single-crystal electronic spectra were recorded with the apparatus previously described.[12] Nicol prisms in both the sample and reference compartment were used as polarizers.

## Results and Discussion

The spectra were recorded on the (010) face, with the electric vector of the incident radiation parallel to the *a* and *c* crystal axes, respectively. If the Co–N direction is assumed as the molecular *z* axis, the square of the projection of *z* on *a* is 0.02, while on *c* it is 0.66. Therefore, if, for the sake of simplicity, the symmetry of the ligand field is assumed as tetragonal, the former spectra yield the perpendicular (⊥) polarization, while the latter give to a good approximation the parallel (‖) polarization. The spectra recorded for a thick and a thin crystal are shown in Figure 1. The spectra of the thick crystal were used for studying the lowest energy band at ≃8000 cm$^{-1}$. Its polarization properties are not so marked. On cooling the maximum is practically not shifted. The band at 13 500 cm$^{-1}$ at room temperature moves to 14 900 cm$^{-1}$ at 4.2 K, appearing ⊥ polarized. The next band shows a peak and a shoulder at room temperature, at 17 400 and 18 800 cm$^{-1}$, while at 4.2 K two maxima are shown at 17 000 and 18 800 cm$^{-1}$. No neat polarization is observed in this case, but

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**Table I.** Assignment of the Absorption Maxima of $Co_2(bz)_4(quin)_2$ to the Electronic Transitions[a]

| ground state | excited state | band maxima[b] | | polarization |
|---|---|---|---|---|
| | | 293 K | 4.2 K | |
| $A_2$, E | E | 8.1 | 8.1 | ∥, ⊥ |
| | $B_1$ | 13.5 | 14.9 | ⊥ |
| | E | 17.4 | 17.4 | ∥, ⊥ |
| | | 18.8 | 18.8 | ∥, ⊥ |
| | $A_2$ | 22.1 | 23.3 | ⊥ |

[a] The orbital levels are those appropriate to $C_{4v}$ symmetry for a monomeric moiety.[14] [b] In $cm^{-1} \times 10^3$.

the spectrum is slightly more intense. The relative intensities of the band at room and liquid helium temperature was estimated as 0.9 ± 0.2. The band with a maximum at 22 100 $cm^{-1}$ at room temperature is neatly ⊥ polarized, and it shifts to 23 000 $cm^{-1}$ at 4.2 K. In the ∥ polarization the band shows also two shoulders at 22 500 and 23 800 $cm^{-1}$. The intensity ratio between room and liquid helium temperature was estimated as 0.80 ± 0.15.

The diffuse reflectance spectra of $Co_2(bz)_4(quin)_2$ were interpreted by Thornton[13] on the basis of the monomeric square-pyramidal moiety. He noticed that the spectra correspond quite closely to those of $[Co(MePh_2AsO)_4NO_3]NO_3$ reported by Gerloch[14] and assigned them accordingly as shown in Table I. Our results show that also the polarization properties of the present compound are similar to those of $[Co(MePh_2AsO)_4NO_3]NO_3$, in the sense that several bands do not show marked polarization properties, a fact which was interpreted as due to the presence of a ground state which is an admixture of $^4A_2$ and $^4E$ terms.[14] The single-crystal spectra therefore must be interpreted in the same way, as shown in Table I. It must be concluded that the energy level pattern of the dimer is quite similar to that of the monomer. Another support to this statement is the observed constancy of the intensities of the electronic transitions with temperature.

As previously noted,[10] the variation of the magnetic moment in the range 300–77 K suggests that the spin state is changed on lowering of the temperature. Large spin–orbit coupling effects are expected in cobalt(II) complexes, which can yield an $S = {}^1/_2$ ground level at low temperature.[15] Therefore a simple exchange Hamiltonian treatment is not possible in this case[11,16,17] and a $J$ value cannot be given. Preliminary ESR data at 4.2 K show the presence of hyperfine split signals[11,18] suggesting that the paramagnetic species achieve magnetic dilution at low temperatures. Therefore we feel confident to assume that a diamagnetic $S = 0$ spin state is the dominant species at 4.2 K. The fact that the electronic spectra do not change so dramatically suggests that the orbital levels are not much affected by the change in the spin state and that the variation is essentially a spin flip. Therefore, the present results give support to those models which predict small splittings of the orbital energy levels due to the interaction between the two halves of the dimer. An angular overlap model we have suggested recently appears promising in this respect.[19,20] Although the splitting of the orbitals of the two metal centers can have small effects on the electronic spectra since the bands are in general broad with half-widths on the order of $10^3$ $cm^{-1}$ (we have calculated[20] splittings of the levels at most of $10^3$ $cm^{-1}$), they are of paramount importance in determining the spin state and as a consequence the magnetic properties.

Another point of interest in our present data is that only two bands show appreciable high-frequency shifts on cooling, and both of them are assigned to transitions to orbitally nondegenerate levels and are ⊥ polarized. Thornton[13] suggested that the blue shift was due to the relative slope of the ground and of the $A_2$ and $B_1$ levels on the basis of the diagrams by Ciampolini and Bertini.[21] The high-frequency shift should be due, therefore, to the bond contraction expected on cooling the crystal. Although this effect can be of importance, it is by no means common to observe such large shifts in monomeric compounds, and as a matter of fact it was not observed by Gerloch.[14] It is possible, therefore, that these transitions are most sensitive to the different populations of the high-spin and low-spin states.

The data now reported show that all the d–d transitions of the present cobalt(II) dimeric carboxylate occur at the same frequencies as in the corresponding monomeric moieties. Therefore the previous results[8] on copper(II) carboxylates are also confirmed, and support is given to the models which justify the magnetic properties considering as negligible the direct metal–metal interaction.

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## Nitrogen-15 Chemical Shifts for Imidazole in Aqueous $Cd^{2+}$ Solutions[1]

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In a recent publication,[3] we reported that complexation of doubly labeled imidazole by $Zn^{2+}$ in aqueous solution leads to significant upfield shifts of the $^{15}N$ resonance relative to neutral, aqueous imidazole. That work also demonstrated that the average $^{15}N$ shift for all ligands in a specific $ZnIm_i^{2+}$ ($i$ = 1–6) species is, to a limited extent, dependent upon $i$.

Results of a similar investigation with aqueous $Cd(NO_3)_2$ solutions containing doubly $^{15}N$-labeled imidazole (the experimental details are exactly as described in the earlier $Zn^{2+}$ study,[3] the only exception being substitution of Mallinckrodt AR $Cd(NO_3)_2 \cdot 4H_2O$ in place of Baker AR $Zn(NO_3)_2 \cdot 6H_2O$ as the source of diamagnetic cation) are summarized in Table

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