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] 293 K	band maxima[b] 4.2 K	polarization
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.

Acknowledgment. Thanks are due to Professor L. Sacconi and Professor I. Bertini for helpful discussion.

Registry No. $Co_2(bz)_4(quin)_2$, 41188-29-8.

References and Notes

(1) R. Tsuchida and S. Yamada, *Nature (London)*, **176**, 1171 (1955); **178**, 1192 (1956); **181**, 479 (1958); **182**, 1230 (1958).
(2) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **17**, 222 (1961).
(3) M. L. Tonnet, S. Yamada, and I. G. Ross, *Trans. Faraday Soc.*, **60**, 840 (1964).
(4) G. F. Kokoszka and H. C. Allen, *J. Chem. Phys.*, **42**, 3693 (1965).
(5) G. W. Reimann, G. F. Kokoszka, and G. Gordon, *Inorg. Chem.*, **4**, 1082 (1965).
(6) A. E. Hansen and C. J. Ballhausen, *Trans. Faraday Soc.*, **61**, 631 (1965).
(7) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966).
(8) L. Dubicki, *Aust. J. Chem.*, **25**, 1141 (1972).
(9) J. Catterick, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 223 (1977).
(10) J. Drew, M. B. Hursthouse, P. Thornton, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 52 (1973).
(11) J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, **20**, 291 (1977).
(12) I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, **15**, 203 (1976).
(13) J. Catterick and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1634 (1976).
(14) M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc. A*, 328 (1970).
(15) R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Am. Chem. Soc.*, **98**, 685 (1976).
(16) M. E. Lines, *J. Chem. Phys.*, **55**, 2977 (1971); **57**, 1 (1972).
(17) A. P. Ginsberg, *Inorg. Chim. Acta, Rev.*, **5**, 45 (1971).
(18) Unpublished results of our laboratory.
(19) A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, in press.
(20) A. Bencini, D. Gatteschi, and L. Sacconi, *Inorg. Chem.*, in press.
(21) M. Ciampolini and I. Bertini, *J. Chem. Soc. A*, 2241 (1968).

Contribution from Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico 87545,
and the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

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

Mohammed Alei, Jr.,*[2a] William E. Wageman,[2a]
and Leon O. Morgan[2b]

Received April 27, 1978

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

0020-1669/78/1317-3314$01.00/0

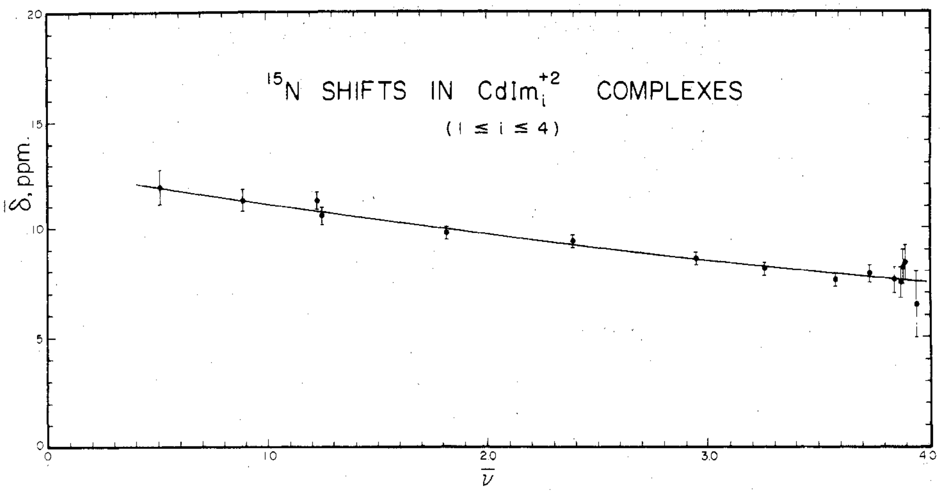

Figure 1. Average ^{15}N shift for a bound imidazole ($\bar{\delta}$) vs. average number of imidazoles bound by a Cd^{2+} ($\bar{\nu}$) for $CdIm_i^{2+}$ complexes in aqueous solution at 25 °C.

Table I

total imidazole concn, mol/L	total added HNO_3 concn, mol/L	total $Cd(NO_3)_2$ concn, mol/L	obsd ^{15}N shift, δ_{obsd}[a]	$\bar{\nu}$
1.7690	0.0455	0.0447	1.45	3.95
0.9283	0.0473	0.0463	3.23	3.90
0.9232	0.0470	0.0466	3.19	3.89
0.8329	0.0486	0.0476	3.48	3.88
0.7081	0.0478	0.0473	4.07	3.85
0.4948	0.0487	0.0479	5.92	3.74
0.3788	0.0491	0.0483	7.52	3.58
0.2871	0.0494	0.0487	9.87	3.26
0.2419	0.0496	0.0488	11.54	2.95
0.1898	0.0498	0.0490	13.94	2.39
0.1502	0.0499	0.0491	16.19	1.82
0.1163	0.0501	0.0492	19.03	1.25
0.1151	0.0501	0.0492	19.48	1.23
0.0967	0.0501	0.0493	21.28	0.89
0.0761	0.0500	0.0495	24.41	0.51

[a] All shifts are diamagnetic (upfield) relative to neutral aqueous imidazole. For all solutions only a single ^{15}N resonance was observed indicating rapid exchange of imidazole between all solution species. All shift measurements were made at 25 ± 0.2 °C.

I and in Figure 1. Analysis of those data, using the reported stepwise formation constants of Tanford and Wagner[4] ($\log K_1 = 2.80$, $\log K_2 = 2.10$, $\log K_3 = 1.55$, $\log K_4 = 1.13$) at 25 °C, $\mu = 0.16$, and $pK_a = 7.12$, gives an average shift value, $\bar{\delta}$, for each coordinated imidazole, and a corresponding value of $\bar{\nu}$, the average number of imidazoles bound by a given Cd^{2+} ion, as shown in Figure 1. The necessary relations are

$$\bar{\nu} = ([TL] - [LH] - [L])/[TM] \tag{1}$$

where [TL] = total imidazole concentration in all forms, [LH] = equilibrium concentration of imidazolium ions, [L] = equilibrium concentration of neutral, noncoordinated imidazole, and [TM] = total Cd^{2+} concentration in all forms. In eq 2, f_{LH} = fraction of total imidazole in the form of imidazolium ion = [LH]/[TL] and f_i = fraction of total imidazole in the form of the species $CdIm_i^{2+} = i[CdIm_i^{2+}]/[TL]$.

$$\bar{\delta} = (\delta_{obsd} - 31.2 f_{LH})/\sum_i (f_i) \tag{2}$$

The numerical factor 31.2 is the diamagnetic shift (in ppm) for the ^{15}N resonance in imidazolium ion relative to that in neutral imidazole[3] which is the reference for all ^{15}N shifts in this work. Equation 2 assigns a shift contribution of $\bar{\delta}$ to any imidazole coordinated to Cd^{2+}, regardless of the particular $CdIm_i^{2+}$ species in which the ligand is found. The trend to lower values of $\bar{\delta}$ for larger values of $\bar{\nu}$ reflects a decreasing shift with increasing imidazole coordination in a given species. To show that explicitly the observed chemical shift (δ_{obsd}) may be expressed as a summation over all species

$$\delta_{obsd} = 31.2 f_{LH} + \sum_1^4 \delta_i^\circ f_i \tag{3}$$

where δ_i° is the average ^{15}N shift for an imidazole in the species $CdIm_i^{2+}$. Best values for the δ_i° may then be found by a least-squares fit to the data for all samples. In this instance, the values found are $\delta_1^\circ = 12.4 \pm 0.5$, $\delta_2^\circ = 10.1 \pm 0.6$, $\delta_3^\circ = 8.7 \pm 0.6$, and $\delta_4^\circ = 7.5 \pm 0.3$, all in ppm upfield from neutral aqueous imidazole, with standard deviations based on the least-squares fit. The solid curve in Figure 1 is for those values, according to

$$\bar{\delta} = \sum_1^4 \delta_i^\circ f_i / \sum_1^4 f_i \tag{4}$$

and indicates the adequacy and consistency of the several parameters, given the published stepwise formation constants.

Significant results of this work include the following: (1) Coordination to Cd^{2+} produces an observed 8–12 ppm diamagnetic shift in the ^{15}N resonance of imidazole (averaged between the two equivalent sites) relative to neutral aqueous imidazole (at pH 9–12). (2) Shift data for Cd^{2+}–imidazole solutions give no evidence for coordination of more than four imidazole groups within the range of compositions employed (0.0261–1.7235 mol/L of total neutral imidazole), whereas for Zn^{2+} it was found necessary to include six species to account properly for the data.[3] (3) Calculated values of δ_i° decrease with increasing i, following the reported decrease in overall formation constants. A similar correspondence between the trends in δ_i° and $\log K_i$ was also indicated for the $ZnIm_i^{2+}$ system.[3] This suggests a possible general correlation between the magnitudes of the ^{15}N NMR shift and the free energy of replacement of H_2O by imidazole in the first sphere of diamagnetic cations. In view of the limited data available, further speculation on the exact nature of the correlation seems premature.

Registry No. Cd^{2+}, 22537-48-0; Im, 288-32-4.

References and Notes

(1) This work was performed under the auspices of the U.S. Department of Energy.
(2) (a) Los Alamos Scientific Laboratory. (b) The University of Texas at Austin.
(3) M. Alei, Jr., L. O. Morgan, and W. E. Wageman, *Inorg Chem.*, **17**, 2288 (1978).
(4) Charles Tanford and Myron L. Wagner, *J. Am. Chem. Soc.*, **75**, 434 (1953); see also Norman C. Li, James M. White, and Edward Doody, *ibid.*, **76**, 6219 (1954).