Table VI. Thermodynamic Parameters for the Reduction of $Co(NSSN)X_2{}^{n+}$ Complexes[a]

complex	k_t, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
$Co(NSSN)Cl_2{}^+$	1.66	10.5	−22.4	17.2
$Co(NSSN)C_2O_4{}^+$	1.65	11.3	−19.8	17.2
$Co(NSSN)(N_3)_2{}^+$	0.145	17.1	−5.2	18.6
$Co(NSSN)Br_2{}^+$	0.097	12.1	−22.9	18.9

[a] $t = 25$ °C, $\Sigma[ClO_4{}^-] = 1.0$ M, $HClO_4$–$LiClO_4$ medium.

The iron(II) reduction rates for $Co(NH_3)_4XY^{n+}$ and $Co(en)_2XY^{n+}$ type complexes follow a general rate pattern $N_3{}^- \gg Cl^- > Br^- > C_2O_4{}^{2-}$, whereas in this series we find $Co(NSSN)Cl_2{}^+$ (1.66) $\sim$ $Co(NSSN)C_2O_4{}^+$ (1.65) $\gg$ $Co(NSSN)(N_3)_2{}^+$ (0.145) $> Co(NSSN)Br_2{}^+$ (0.085), where k_t, in M^{-1} s^{-1}, is given in parentheses. The most interesting facet is the nonreactivity of the diazido complex. Each of the other NSSN complexes is reduced by iron(II) at rates from 10^2 to 10^4 times more rapid than those of the most closely related tetraammine and/or bis(ethylenediamine) complex. A similar rate enhancement would be expected for $Co(NSSN)(N_3)_2{}^+$. Note also the anomalous $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the diazido complex (Table VI). These observations, in conjunction with the minor acid dependence (medium effect), point to a system which is particularly sensitive to solvent participation, ion-pairing, or bond-cleavage effects.

Registry No. s-cis-$Co(NSSN)(N_3)_2{}^+$, 46751-04-6; s-cis-$Co(NSSN)Cl_2{}^+$, 32594-33-5; s-cis-$Co(NSSN)C_2O_4{}^+$, 38586-91-3; s-cis-$Co(NSSN)Br_2{}^+$, 46135-49-3; Fe^{2+}, 15438-31-0.

References and Notes

(1) For a general review see: (a) G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971); (b) J. H. Worrell, T. E. MacDermott, and D. H. Busch, *Chem. Commun.*, 661 (1969); (c) R. W. Hay, P. M. Gidney, and G. A. Lawrance, *J. Chem. Soc., Dalton Trans.*, 779 (1975).

(2) For a general review see: (a) J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.*, 5, 7 (1971); (b) J. M. Palmer and E. Deutsch, *Inorg. Chem.*, 14, 17 (1975), and references therein; (c) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *ibid.*, 12, 2690 (1973).

(3) J. H. Worrell, *Inorg. Chem.*, 14, 1699 (1975).

(4) (a) R. H. Lane and L. E. Bennett, *J. Am. Chem. Soc.*, 92, 1089 (1970); (b) J. H. Worrell and T. A. Jackman, *ibid.*, 93, 1044 (1971); (c) J. H. Worrell, R. A. Goddard, E. M. Gupton, and T. A. Jackman, *Inorg. Chem.*, 11, 2734 (1972); (d) C. Shea and A. Haim, *J. Am. Chem. Soc.*, 93, 3055 (1971); (e) R. H. Lane and L. E. Bennett, *Chem. Commun.*, 491 (1971); (f) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, 15, 139 (1976).

(5) 1,8-Diamino-3,6-dithiaoctane = $NH_2CH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$ and is abbreviated in this manuscript as (NSSN), as in, e.g., $Co(NSSN)(N_3)_2{}^+$.

(6) (a) A. Haim, *J. Am. Chem. Soc.*, 85, 1016 (1963); (b) A. Haim, *ibid.*, 86, 2352 (1964); (c) P. Benson and A. Haim, *ibid.*, 87, 3826 (1965).

(7) W. J. Blaedel and B. W. Meloche, "Elementary Quantitative Analysis", 2nd ed, Harper and Row, New York, N.Y., 1963, p 473.

(8) (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 67, 1425 (1963); (b) T. W. Newton and F. B. Baker, *Inorg. Chem.*, 4, 1166 (1965).

(9) R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, 87, 5597 (1965).

(10) D. E. Pennington and A. Haim, *Inorg. Chem.*, 6, 2138 (1967).

(11) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, 91, 3769 (1969).

(12) R. V. James and E. King, *Inorg. Chem.*, 9, 1301 (1970).

(13) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 10, 2635 (1971).

(14) C. Lavallee and E. Deutsch, *Inorg. Chem.*, 11, 3133 (1972).

(15) M. K. Loar, J. C. Thomas, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, 16, 2877 (1977).

(16) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed, Reinhold, New York, N.Y., 1958, p 585 ff.; see also 2nd ed, 1950, pp 459, 472.

(17) $\ln k_t = \ln k^H - n\alpha[M^{n+}]$, where k^H corresponds to the value of k_t in pure $HClO_4$, n is the cation charge of the supporting electrolyte, and α is a constant having a value presumably <0.1 for $LiClO_4$–$HClO_4$ systems obeying Harned's rule.[8a] For comparative information, the data in Tables II and IV give the following. $LiClO_4$: $\alpha = 0.198 \pm 0.01$ M^{-1} and $k^H = 0.152 \pm 0.001$ M^{-1} s^{-1}. $Ba(ClO_4)_2$: $\alpha = 0.212 \pm 0.02$ M^{-1} and $k^H = 0.164 \pm 0.002$ M^{-1} s^{-1}.

(18) H. Taube, *Can. J. Chem.*, 37, 129 (1959).

(19) B. Bosnich, W. R. Keen, and A. T. Phillip, *Inorg. Chem.*, 8, 2567 (1969).

(20) R. A. Goddard and J. H. Worrell, *Inorg. Chem.*, 16, 1249 (1977).

## Selective Crown Ether Assistance in Ligand-Exchange Reactions of Transition-Metal Complexes

Gary L. Blackmer,[*1a] Mark D. Nordyke,[1a] Thomas M. Vickrey,[1b] Richard A. Bartsch,[1a] and Robert A. Holwerda[1a]

Cation complexation by crown ethers (macrocyclic polyethers) has been an area of intense interest for the last decade.[2a] Complexation studies for a wide variety of inorganic and organic cations have appeared.[2,3] Less familiar is the association of crown ethers with neutral, but polar, molecules.[3,4] One of the best examples of such association is the formation of an acetonitrile–crown ether adduct or "complex" of variable stoichiometry[5] which is utilized in the purification of 18-crown-6, **1**. It seemed reasonable that a similar crown
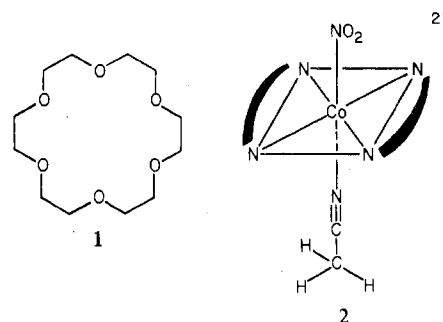
ether–acetonitrile association might enhance the exchange reactions of acetonitrile ligands from transition-metal complexes. We now report the first example of such crown ether assisted ligand exchange.

Clarkson and Basolo[6] previously observed changes in the ^1H NMR spectrum of *trans*-nitrobis(ethylenediamine)-acetonitrilocobalt(III) perchlorate, $[Co(en)_2(CH_3CN)-NO_2][ClO_4]_2$, **2**, when the solid was dissolved in D_2O (buffered at pD 4.4) and allowed to stand in the spectrometer probe at ambient temperature. The ^1H NMR spectrum of **2** initially exhibited a methyl resonance positioned at 2.1 ppm upfield from the HOD resonance. After the solution was allowed to stand, this methyl resonance slowly decreased in intensity and a new, permanent, single-line resonance located 2.6 ppm upfield from HOD simultaneously emerged. The ^1H NMR resonance of added excess acetonitrile superimposed perfectly upon that of the reaction product. Thus, the ^1H NMR spectral changes indicated a slow aquation of **2**, the bound acetonitrile being replaced by solvent (eq 1). Additional support for this
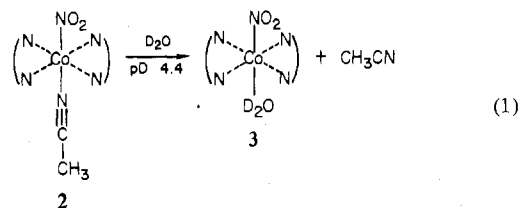
interpretation was provided by the ultraviolet–visible absorption spectrum of the reaction product which was identical with that of **3** prepared by an alternative procedure. Therefore, ^1H NMR spectra appeared to be an ideal method for measuring the kinetics of acetonitrile removal from the cobalt ion coordination sphere of **2** and assessing the effect, if any, of crown
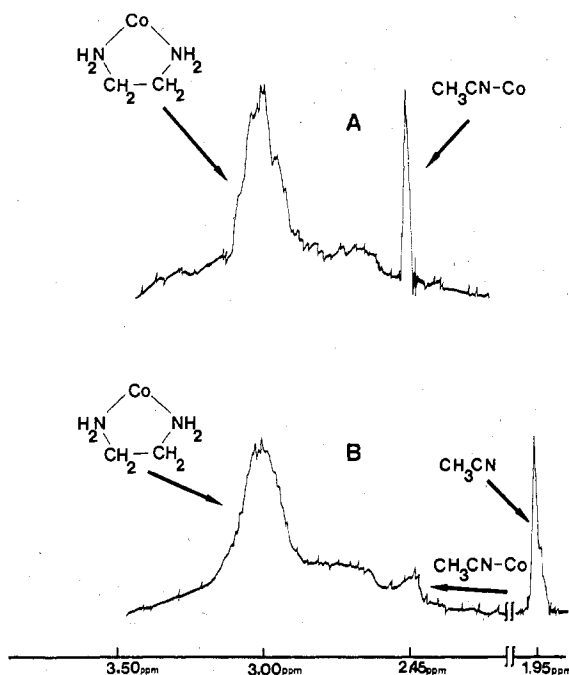
Figure 1. ^{1}H NMR spectra: (A) spectrum of a freshly prepared D_2O solution of $[Co(en)_2(CH_3CN)NO_2]^{2+}$ at 20 °C and pD 4.4; (B) spectrum of sample in spectrum A at t_∞.

Figure 2. Logarithmic plot of $(I_t - I_\infty)$ vs. time.

ethers upon this substitution process.

Results

Aquation of 2 in the Absence of Crown Ethers. Conditions employed in this study of the aquation of $[Co(en)_2-(CH_3CN)(NO_2)]^{2+}$ were the same as those outlined by Clarkson and Basolo.[6] Figure 1A illustrates the ^{1}H NMR spectrum of a freshly prepared D_2O solution of the cobalt–acetonitrile complex, buffered at pD 4.4 (see Experimental Section), at a time when less than 10% of the complex had reacted.

The broad resonance centered at 1.5 ppm upfield from HOD is attributed to the methylene protons of the coordinated ethylenediamine ligands. The breadth of this signal is due, at least in part, to spin coupling of the protons to the long-lived nuclear spin states of cobalt-59 ($I = {}^7/_2$, 100% abundant).[7] Additional line width of this resonance may be ascribed to the fluctional character of the ethylenediamine ring system.[8]

The sharp, single-line resonance located at 2.1 ppm upfield from HOD is assigned to the methyl resonance of the cobalt-bound acetonitrile ligand. The rate of the aquation reaction was monitored by observing the gradual decrease of the integral of this peak as a function of time (I_t). Upon completion of the aquation reaction (t_∞), a ^{1}H NMR spectrum of the type shown in Figure 1B was observed. The new resonance, that of the free acetonitrile methyl group, appeared at a position 2.6 ppm upfield from HOD concomitantly with the disappearance of the 2.1-ppm resonance line. This new peak could also have been used to study the exchange kinetics.

Plots of log $(I_t - I_\infty)$ vs. time were found to be linear for both the unassisted and crown ether assisted aquation reactions (Figure 2). Observed first-order rate constants (k_{obsd}) were obtained from the linear least-squares slopes of these plots. Rate data collected at several temperatures for the unassisted aquation of *trans*-$[Co(en)_2(NO_2)(CH_3CN)]^{2+}$ are presented in Table I. Activation parameters for this reaction at pD 4.4 ($\Delta H^* = 19.4 \pm 1.4$ kcal/mol; $\Delta S^* = -8 \pm 5$ cal/(mol deg)) were derived from an Eyring plot[9] of the temperature-dependence data. Although the pD was held constant in this series of experiments (pD 4.4), the rate of the aquation reaction
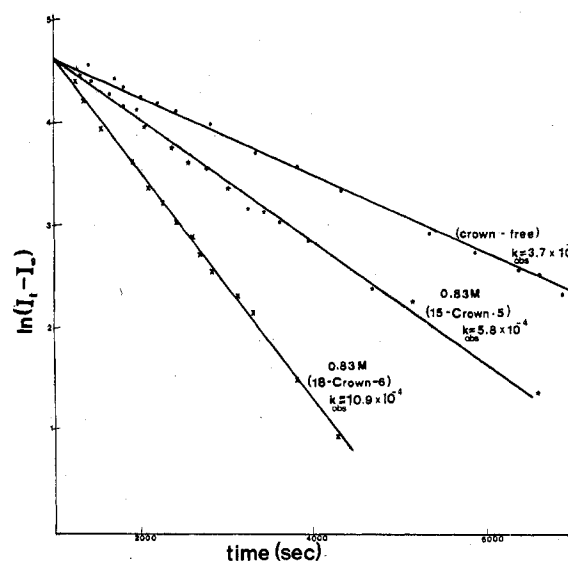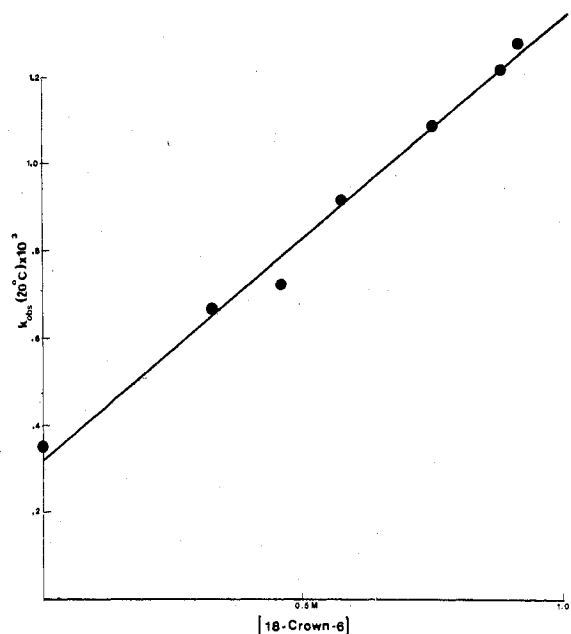

Figure 3. Plot of k_{obsd} vs. [18-crown-6] demonstrating first-order concentration dependence.

Table I. Observed First-Order Rate Constants, k_{obsd}, for the Aquation of $[Co(en)_2(CH_3CN)NO_2]^{2+}$ at pD 4.4 as a Function of Temperature

| $t,^a$ °C	$10^4 k_{obsd}$, s^{-1}	$t,^a$ °C	$10^4 k_{obsd}$, s^{-1}
10	1.53 ± 0.55	30	12.8 ± 0.5
20	3.74 ± 0.50	40	44.9 ± 0.2

^{a} The uncertainty in temperature is estimated at ±0.5 °C.

was determined to be essentially pD independent over a 10^5-fold range in deuterium ion concentration.

Aquation of *trans*-$[Co(en)_2(NO_2)(CH_3CN)]^{2+}$ in the Presence of 18-Crown-6. In view of its ability to form complexes with acetonitrile, 18-crown-6 was chosen to probe the influence of crown ethers on the dynamics of the ligand-exchange process of the acetonitrilecobalt(III) complex **2**. Observed rate constants for the aquation of *trans*-$[Co(en)_2(NO_2)(CH_3CN)]^{2+}$ in the presence of crown ether **1** increase linearly with increasing [18-crown-6] (Figure 3). Thus, the data are consistent with the rate law

$$-d[Co(en)_2(NO_2)(CH_3CN)^{2+}]/dt =$$
$$(k_0 + k_1[18\text{-crown-}6])[Co(en)_2(NO_2)(CH_3CN)^{2+}] =$$
$$k_{obsd}[Co(en)_2(NO_2)(CH_3CN)^{2+}]$$

with $k_0 = (3.2 \pm 0.9) \times 10^{-4}$ s^{-1} and $k_1 = (8.7 \pm 0.2) \times 10^{-4}$ M^{-1} s^{-1} at 20 °C. The k_0 value agrees well with the rate constant obtained for the unassisted aquation reaction under the same conditions (($3.7 \pm 0.5) \times 10^{-4}$ s^{-1}).
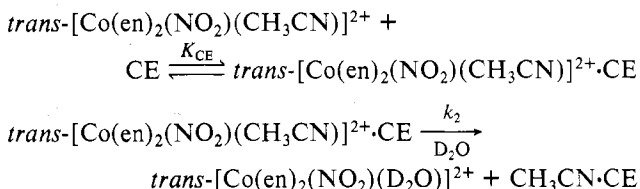
Aquation of 2 in the Presence of 15-Crown-5. In an attempt to investigate the nature of the crown ether–acetonitrile interaction in the aquation of **2**, a crown ether with a smaller cavity, 15-crown-5, **4**, was used. Figure 2 indicates that under

4
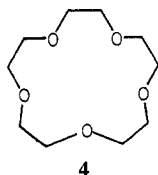
identical conditions **4** is about half as effective as **1** in assisting the removal of acetonitrile from the coordination sphere of the cobalt ion. The aquation of **2** also exhibited rate enhancement with increasing [**4**], but the effect was much less pronounced than with **1**.

Discussion

Our kinetic data for the crown ether assisted aquation of *trans*-[Co(en)$_2$(NO$_2$)(CH$_3$CN)]$^{2+}$ are consistent with a mechanism involving rapid preequilibrium complex formation between the crown ether (abbreviated CE) and cobalt(III)-complexed acetonitrile followed by rate-limiting dissociation of the Co–NCCH$_3$ linkage within this complex:

$$trans\text{-}[Co(en)_2(NO_2)(CH_3CN)]^{2+} +$$
$$CE \xrightleftharpoons{K_{CE}} trans\text{-}[Co(en)_2(NO_2)(CH_3CN)]^{2+}\cdot CE$$

$$trans\text{-}[Co(en)_2(NO_2)(CH_3CN)]^{2+}\cdot CE \xrightarrow[D_2O]{k_2}$$
$$trans\text{-}[Co(en)_2(NO_2)(D_2O)]^{2+} + CH_3CN\cdot CE$$

The rate law predicted on the basis of this mechanism is

$$\frac{-d[Co(en)_2(NO_2)(CH_3CN)^{2+}]_{tot}}{dt} =$$
$$\frac{k_2 K_{CE}[CE][Co(en)_2(NO_2)(CH_3CN)^{2+}]_{tot}}{1 + K_{CE}[CE]}$$

where $[Co(en)_2(NO_2)(CH_3CN)^{2+}]_{tot}$ represents the sum of the concentration of the free acetonitrilecobalt(III) complex and the corresponding cobalt(III) acetonitrile–crown ether adduct. This rate law reduces to the experimentally observed form when $K_{CE}[CE] << 1$. Considering the 18-crown-6 concentration range covered in the rate studies, we estimate an upper limit of 0.1 M^{-1} for K_{CE} at 20 °C. Larger K_{CE} values would be expected for reactions conducted in aprotic solvents. Generally, crown ether interactions of the type under consideration here are considerably attenuated when allowed to occur in protic solvents such as water. Although many applications of crown ethers in inorganic and organic chemistry have been reported, this is, to our knowledge, the first example of a crown ether facilitated removal of a ligand from the first coordination sphere of a transition-metal complex. Although the rate enhancement (as a function of crown ether concentration) is relatively small, it is definite. It could be argued that simple medium effects are responsible for these accelerated rates of hydrolysis. However, this idea seems to be ruled out when a comparison of the observed aquation rates is made

between the various crown ethers employed (Figure 2). Equal concentrations of 18-crown-6 and 15-crown-5 should exhibit virtually identical medium effects and therefore give rise to identical rate enhancements if the medium effect were indeed the predominant influence controlling the aquation rates. Clearly, this is not the case.

Cram and co-workers[10] have postulated a three-point binding model for the complexation of *tert*-butylammonium ions by crown ethers **5**. Supporting evidence for this model

5
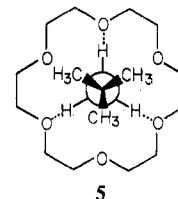
has been obtained from the X-ray crystal structure of a crown ether complex.[11] Less efficient complexation of alkyl ammonium ions by **4** than **1** would be anticipated because of the poorer fit of the three-point binding model with the smaller crown ether. Hydrogen bonding (C—H···O) of malononitrile to 18-crown-6 has recently been demonstrated in the X-ray crystal structure of the malononitrile adduct of 18-crown-6.[12] Therefore, an entirely analogous situation exists for the complexation of cobalt-bound acetonitrile in **2** in which the acidic methyl group C–H bonds are utilized for binding to the crown ether. It seems likely, then, that a smaller K_{CE} value partially accounts for the reduced aquation rate enhancement observed for 15-crown-5 compared with that for 18-crown-6.

Experimental Section

Instrumentation. Proton NMR spectra were recorded on a Varian XL-100/15 spectrometer equipped with a Varian V-6040 temperature controller and an external (^{19}F) lock and an internal (^{2}H) pulse-lock circuit. A du Pont 310 curve resolver was employed to confirm integral accuracy.

Preparation of Nitrosylbis(ethylenediamine)cobalt(III) Perchlorate, [Co(en)$_2$NO](ClO$_4$)$_2$. The complex was prepared by the method of Feltham and Nyholm.[13]

Preparation of *trans*-Nitrobis(ethylenediamine)acetonitrilocobalt(III) Perchlorate, *trans*-[Co(en)$_2$(CH$_3$CN)(NO$_2$)](ClO$_4$)$_2$. The complex was prepared by the method of Clarkson and Basolo.[6] Elemental analysis of this complex corresponded to previously reported literature values.[6]

Preparation of 18-Crown-6. The method of Gokel et al.[5] was used to prepare the crown ether 18-crown-6. The desired high purity of the crown ether was achieved by successive recrystallizations of the crown ether–acetonitrile adduct followed by complete removal of the acetonitrile under high vacuum. The criterion for complete removal of acetonitrile was the total absence of the methyl resonance in the 100-MHz proton NMR spectrum of a solution of the crown ether in DCCl$_3$.

Aquation of the Nitrobis(ethylenediamine)acetonitrilocobalt(III) Cation, [Co(en)$_2$(CH$_3$CN)(NO$_2$)]$^{2+}$. Kinetic experiments were performed at 10, 20, 30, and 40 °C. The pD was originally buffered at 4.4 with potassium hydrogen phthalate in the D$_2$O solution. The temperature within the probe was calibrated at each temperature by observing the frequency difference between the centers of the quartet and doublet patterns in a neat methanol sample. The kinetics of aquation were monitored by observing the decrease in integral intensity of the cobalt-bound acetonitrile methyl resonance. The peak occurs 2.10 ppm upfield from HOD.

In general, the kinetic experiments were performed as follows. Approximately 37 mg of solid [Co(en)$_2$(CH$_3$CN)(NO$_2$)](ClO$_4$)$_2$ was placed in a 5-mm NMR tube. The buffered D$_2$O solution (1.0 mL), which was previously thermostated in a constant-temperature water bath, was added and the resulting solution then placed in the thermostated NMR probe. The NMR spectrometer was offset at 86 201 Hz, 4095 Hz from the center band of the ^{1}H resonant frequency. The kinetic runs were monitored using either the deuterium lock signal from the D$_2$O solvent (at 15.4 MHz) or the external ^{19}F lock signal at 94.2 MHz. The integral of the methyl resonance of

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_∞ 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$_3$CN)$_2$-(NO$_2$)](ClO$_4$)$_2$ was added 1.0 mL of a D$_2$O 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.

Registry No. **1**, 17455-13-9; **2**, 61046-67-1; **4**, 33100-27-5.

References and Notes

(1) (a) Texas Tech University. (b) Texas A&M University.
(2) (a) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974), and references therein; (b) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
(3) D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974).
(4) I. Goldberg, *Acta Crystallogr., Sect. B*, **31**, 754 (1975).
(5) G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, **39**, 2445 (1974).
(6) S. G. Clarkson and F. Basolo, *Inorg. Chem.*, **12**, 1528 (1973).
(7) J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, **10**, 2010 (1971).
(8) J. L. Sudmeier, G. L. Blackmer, C. H. Bradley, and F. A. Anet, *J. Am. Chem. Soc.*, **94**, 757 (1972), and references therein.
(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, Chapter 6, p 461.
(10) E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel, T. L. Tarnowski, S. S. Moore, and D. J. Cram, *J. Am. Chem. Soc.*, **99**, 2564 (1977).
(11) I. Goldberg, *Acta Crystallogr., Sect. A*, **31**, 5166 (1975).
(12) R. Haufmann, A. Knoechel, J. Kopf, J. Oelher, and G. Rudolph, *Chem. Ber.*, **110**, 2249 (1977).
(13) R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4**, 1334 (1965).
(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.

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(μ-benzoato-O,O')-bis(quinoline)dicobalt(II)

A. Bencini, C. Benelli, and D. Gatteschi*

Received December 29, 1977

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 $\simeq$700 nm was attributed to the d–d transitions, while the band at $\simeq$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(μ-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
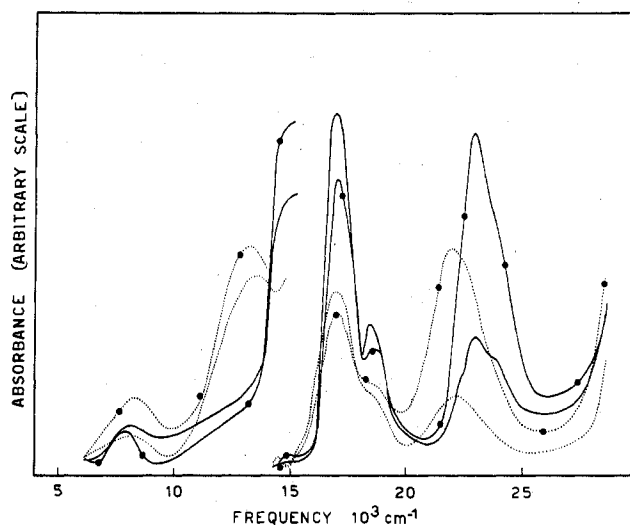

Figure 1. Single-crystal polarized electronic spectra of the Co$_2$-(bz)$_4$(quin)$_2$ complex recorded at 290 K (···) and 4.2 K (—) on the (010) face. The traces with ● are the spectra recorded with the electric vector parallel to *a*; the others have the electric vector parallel to *c*.

from 4.4 μ_B at room temperature to 1.72 μ_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.

Experimental Section

The compound was obtained by addition of a large excess of quinoline to a boiling solution of benzoic acid and Co(BF$_4$)$_2$·6H$_2$O 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 ($\perp$) polarization, while the latter give to a good approximation the parallel ($\parallel$) 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 $\simeq$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 $\perp$ 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