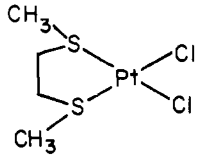
aquation gives 100% of the β-*cis*-chloroaquo complex with the aquo ligand trans to the secondary nitrogen, while the Hg^{2+}-catalyzed reaction gives only trans product.[7] In the absence of unambiguous stereochemical evidence it is not possible to examine the relationship between the steric course and the entropy of activation, but the activation parameters bear a strong resemblance to those of the *trans*-(*RS*)-[Co(2,3,2-tet)Cl_2]$^+$ complex, which aquates with complete retention of configuration. Although there is good reason to believe that the coordinated sulfur atoms are pyramidal (ψ-tetrahedral with the lone pair occupying the fourth position), care must be taken not to carry the analogy relating NH with S too far. The amine nitrogens are configurationally stable provided the N-H bond remains intact whereas the sulfur atom is capable of inversion without the need for any bond rupture. This may be the reason why we have been unable to isolate more than one form of the *trans*-dichloro complex. However, the rate of inversion of a sulfur atom in a similar situation, *i.e.*



has been shown to be fairly slow.[16] It will probably be necessary to await an X-ray diffraction study of the crystalline solids to see (a) whether *trans*-[Co(ETE)Cl_2]$^+$ has the *RS* configuration as predicted and (b) whether the β-*cis*-chloroaquo product has undergone inversion at the sulfur.

The results of the base hydrolysis are also of interest because here there is a considerable difference between the reactivity of the ETE and the 2,3,2-tet complexes, the latter being some 8–20 times more reactive than the former. It has already been shown that the dissociatively active conjugate base from the (*RS*)-2,3,2-tet complex has lost a proton from the secondary amine nitrogen[6] and the lower reactivity of the ETE complex is consistent with the absence of secondary amine protons. The reactivity toward base hydrolysis is closer to that of the *trans*-[Co(en)$_2$$Cl_2$]$^+$ cation (Table V).[17]

Acknowledgment. This work was supported by a grant from the Science Research Council.

Registry No. *trans*-[Co(ETE)Cl_2]ClO_4, 41777-25-7; *cis*-[Co(ETE)ClH_2O]$^{2+}$, 41777-26-8; *trans*-[Co(ETE)ClH_2O]$^{2+}$, 41777-27-9.

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[16] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 992 (1972).

[17] The lone pair on the sulfur does not appear to confer any labilizing properties upon this donor in its thioether form and the comparison should be made with OH_2, which has a lone pair but no significant labilizing power, rather than with NH_2^- (or NR_2^-) which has a lone pair *and* confers considerable lability upon the complex.

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Preparation and Magnetic Properties of Cobalt(II) and Cadmium(II) Complexes of the Dianion of Cyclopentadienedithiocarboxylic Acid

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The disodium salt of cyclopentadienedithiocarboxylic acid reacts with cobalt(II) bromide and cadmium(II) bromide in anhydrous acetonitrile to form 2:1 ligand to metal complexes which can be isolated as the tetraethylammonium salts. The cobalt and cadmium complexes possess D_{2h} symmetry at the metal center as indicated by electron spin resonance, optical, and infrared spectroscopy. The unpaired electron in the low-spin cobalt complex is shown to occupy a molecular orbital made up of the d_{yz} metal orbital. When compared to other cobalt(II) dithiolate systems, this further indicates the strong electron-withdrawing nature of the dithiolate ligand.

Introduction

Much recent interest has centered on the chemistry of transition element dithiolate complexes. The recent synthesis of a novel, new dithiolate ligand, the dianion of cyclopentadienedithiocarboxylic acid, and the characterization of its zinc and copper complexes have prompted the syntheses of further metal complexes.[1] It was hoped the unusual electronic effects at the metal center of this ligand might be further substantiated by an investigation of a wider range of complexes. Complexation of cobalt(II) and cadmium(II) to form dianionic 2:1 species has been achieved.

The synthesis of the cobalt complex was undertaken because of the scarcity of 1,1-dithiolate complexes of cobalt in the +2 oxidation state.[2] Reaction of cobalt(II) with dithiocarbamates leads to oxidation of the metal even under anhydrous and oxygen-free conditions.[3] Since the dithiocarbamates are mononegative species, the dinegative charge on the cyclopentadienedithiocarboxylate ligand was expected to stabilize a cobalt(II) complex.[4]

It was also felt that the electronic and magnetic effects of the ligand might be more fully understood when the properties of the cobalt complex were compared to those of other cobalt(II) dithiolate systems.[5-7]

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[1] P. C. Savino and R. D. Bereman, *Inorg. Chem.*, 12, 173 (1973), and references therein.

[2] D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 294 (1970).

[3] J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, 2, 251 (1966).

[4] Although the cobalt(III) complex of isomaleonitriledithiolate Co[i-$S_2C_2(CN)_2$]$_3^{3-}$ has been prepared, no reference to the synthesis nor attempted synthesis of a cobalt(II) complex exists. One would predict by the same reasoning it should be stable. Attempts are currently under way to prepare a cobalt(II) complex of i-$S_2C_2(CN)_2^{2-}$.

[5] K. M. Erck and B. B. Wayland, *Inorg. Chem.*, 11, 1141 (1972).

[6] E. Paglia, *Gazz. Chim. Ital.*, 87, 1133 (1957).

[7] E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, 86, 926 (1964).

Experimental Section

Materials. Reagent grade carbon disulfide was stored over and distilled from 4-A molecular sieves. Acetonitrile was repeatedly distilled from phosphorus pentoxide. Tetrahydrofuran was stored over 4-A molecular sieves. Pyridine was repeatedly distilled from barium oxide. Cyclopentadiene was prepared by the thermal cracking of dicyclopentadiene.

$CoBr_2$ and $CdBr_2$ were obtained from Research Organic/Inorganic Chemical Corp. $(C_2H_5)_4NBr$ (anhydrous) was obtained from Aldrich Chemical Co.

Experimental Procedure. Sample preparations and reactions were carried out under rigorously anhydrous conditions using Schlenk techniques under a blanket of anhydrous nitrogen gas further purified as before.[1] Yields were low since certain quantities of product were lost with the filtration of NaBr. All solvents were thoroughly degassed before use.

$Na_2C_5H_4CS_2 \cdot C_4H_8O$. This complex was prepared by an improved method of that formerly used.[1] Sodium metal was used in place of sodium hydride as a reducing agent. Apparently impurities in some samples of sodium hydride catalyze the decomposition of the sodium salt of the ligand during its isolation. *Anal.* Calcd for $Na_2C_5H_4CS_2 \cdot C_4H_8O$: C, 46.49; H, 4.68; S, 24.83. Found: C, 46.35; H, 4.70; S, 24.75.

$[(C_2H_5)_4N]_2Co(C_5H_4CS_2)_2$. This complex was prepared in the following manner. Typically, 0.794 g of cobalt bromide, 2.036 g of sodium cyclopentadienedithiocarboxylate, and 1.487 g of tetraethylammonium bromide were added to 200 ml of anhydrous acetonitrile at −70°. This frozen mass was slowly warmed to room temperature with stirring and allowed to react for 1 hr. The sodium bromide formed was removed by filtration and the filtrate was reduced in volume to approximately 30 ml. The dark brown crystals were collected by filtration and dried under vacuum. *Anal.* Calcd for $[(C_2H_5)_4N]_2Co(C_5H_4CS_2)_2$: C, 56.06; H, 8.08; N, 4.67. Found: C, 55.86; H, 8.13; N, 4.67.

$[(C_2H_5)_4N]_2Cd(C_5H_4CS_2)_2$. This bright yellow complex was prepared in a manner analogus to that previously reported for the zinc and copper complexes.[1] *Anal.* Calcd for $[(C_2H_5)_4N]_2Cd(C_5H_4CS_2)_2$: C, 51.47; H, 7.41; N, 4.29. Found: C, 51.62; H, 7.54; N, 4.32.

$[(C_2H_5)_4N]_2Zn(Co)(C_5H_4CS_2)_2$. Samples of the $Co(C_5H_4CS_2)_2{}^{2-}$ unit doped into the corresponding zinc matrix were obtained by simply preparing the zinc complex in the presence of a cobalt impurity under the conditions outlined for the cobalt procedure above. Typically, 0.048 g of $CoBr_2$ and 0.213 g of $ZnBr_2$ served as starting ratios.

Analyses. All analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tenn. The cobalt complex is extremely labile and special sample containers sealed under vacuum were necessary to ensure its stability during transit.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at room temperature using the Gouy method. Again special sample containers were necessary to ensure the stability of the samples. Pascal's constants were used to correct the measurements for diamagnetic contributions of the cation, ligand, and core electrons of the metal.[8]

Spectroscopic Measurements. Infrared spectra were obtained by the use of Nujol mulls and KBr pellets employing a Beckman IR-5A and a Perkin-Elmer Model 457 spectrophotometer. Ultraviolet-visible spectra were obtained in specially constructed quartz cells, which allowed anhydrous solutions to be manipulated, and a Cary Model 14 spectrophotometer. X-Band electron spin resonance spectra were obtained at 300 and 100°K as before.[9] Second-order corrections, as previously described, were employed to correct for perturbations of the Zeeman transitions resulting from hyperfine interactions.[9]

Results and Discussion

Tetraethylammonium bis(cyclopentadienedithiocarboxylato)cobaltate(II) was found to be much more unstable than the corresponding zinc(II), cadmium(II), or copper(II) complexes. The stability of the complexes prepared to date in this laboratory decreases as the number of d electrons of the metal decreases indicating the apparent importance of the electron-withdrawing ability of the ligand in forming stable covalent complexes. The magnetic moment of the cobalt complex is 2.55 BM, characteristic of a low-spin d^7 system of either square-planar or severely distorted tetragonal symmetry.[10,11] The electron spin resonance spectrum of the cobalt(II) complex is indicative of a distorted square-planar environment at the metal. The spin Hamiltonian parameters obtained for the cobalt complex in an acetonitrile glass at 100°K and for the cobalt complex doped into the corresponding zinc matrix are identical (Table I). It is assumed here that the largest g value is g_{xx} and the smallest is g_{zz} as has been found in other cobalt(II) dithiolate systems where single-crystal data were also available.[12,13] It is possible that the Zn complex may not adopt a square-planar coordination with this ligand. However, in the case of the copper complex[1] and again here, it has served as a quite effective lattice. The anisotropic esr spectrum of the cobalt(II) complex shows 3 g values and resolution of at least five of the eight lines (Co: $I = {}^7/_2$) for two of the three sets of nuclear hyperfine interaction lines (Figure 1). The third set is poorly resolved and only an estimation of the A_{yy} value can be made. The anisotropic spectrum indicates the local symmetry at the metal is now D_{2h} or the same as the gross symmetry of the complex. The previously reported copper(II) complex[1] showed only ∥ and ⊥ components in the esr spectrum indicative of a local C_{4v} or D_{4h} environment. This lower symmetry is also indicated by the far-infrared spectrum of the cobalt(II) complexes[1] (Table II). In D_{4h} symmetry, one doubly degenerate E_u mode is anticipated in the metal-sulfur stretch region; while, two nondegenerate modes of B_{2u} and B_{3u} symmetry are expected for a complex with D_{2h} symmetry. Two bands are observed for the cobalt complex while one was observed for the copper and zinc complexes.[1]

Table I. Esr Parameters for $[(C_2H_5)_4N]_2Co(C_5H_4CS_2)_2$

	CH_3CN glass	Zn matrix		CH_3CN glass	Zn matrix
g_{xx}	2.279	2.273	$A_{xx}{}^a$	0.007824	0.008147
g_{yy}	2.051	2.053	A_{yy}	0.00278[b]	0.00245[b]
g_{zz}	1.993	1.988	A_{zz}	0.002239	0.002038

[a] A units are cm^{-1}. [b] Estimated from poorly resolved peaks.

The different effective symmetries of these two complexes at the metal may be explained by the differences in the ionic radii for cobalt(II) and copper(II). For copper(II), it can be expected that the sulfur-sulfur distances in the x and y directions (Figure 2) should be equal so that the copper is surrounded by four equivalent sulfur atoms in the first coordination sphere. The larger ionic radius of cobalt(II) would cause a lengthening of the sulfur-sulfur distances in the y direction (Figure 2) bringing about an anisotropy in the x-y plane. If this hypothesis is valid, the corresponding cadmium complex should also show two metal-sulfur stretches in the infrared spectrum as was observed (Table II).

The lowered local symmetry in the cobalt complex leads to three possible orderings of the d-orbital energy levels (Figure 3). The ordering of the $d_{x^2-y^2}$, d_{yz}, and d_{z^2} atomic orbitals is dependent on the amount of rhombic distortion. In a low-spin d^7 system, two of these three orbitals will be filled while the third will contain a single unpaired electron.

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(8) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

(9) D. P. Johnson and R. D. Bereman, *J. Inorg. Nucl. Chem.*, **34**, 679 (1972).

(10) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 192 (1964).

(11) F. A. Cotton, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 865.

(12) A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).

(13) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

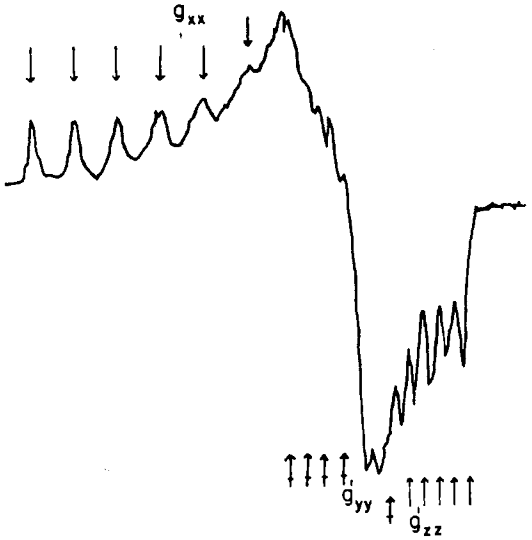

Figure 1. Electron spin resonance spectrum of $Co(C_5H_4CS_2)_2^{2-}$ doped in zinc matrix. Arrows pointing down indicate resolved A_{xx} lines, arrows pointing up are resolved A_{zz} lines, and arrows with crosses indicate estimated positions for A_{yy} lines.

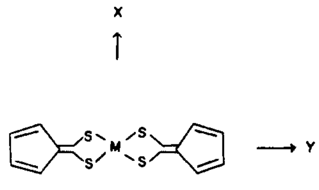

Figure 2. Coordinate system chosen for $M(C_5H_4CS_2)_2^{2-}$.

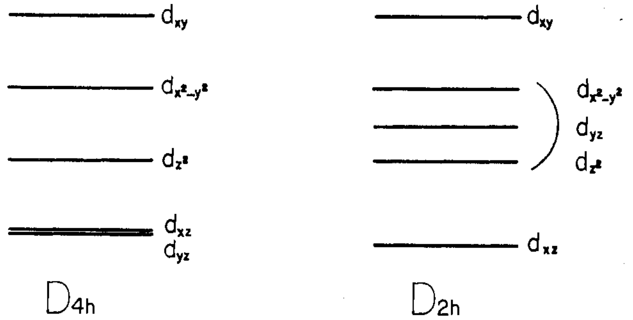

Figure 3. Ordering of d-orbital energy levels in D_{4h} and D_{2h} symmetry using the coordinate system in Figure 2. The amount of rhombic distortion in D_{2h} symmetry determines the relative ordering of the d_{z^2}, $d_{x^2-y^2}$, and d_{yz} orbitals.

Table II. Infrared Spectral Peaks of $[(C_2H_5)_4N]_2M(C_5H_4CS_2)_2$ (cm^{-1})

$[(C_2H_5)_4N]_2Co(C_5H_4CS_2)_2$: 1331 s, 1282 m, 1250 w, 1205 vw, 1170 m, 1060 s, 1030 s, 1000 w, 920 s, 810 s, 780 m, 738 s, 730 m, 700 w, 639 m, *450 m*, *380 s*

$[(C_2H_5)_4N]_2Cd(C_5H_4CS_2)_2$: 1345 s, 1207 m, 1173 s, 1063 m, 1022 m, 1000 m, 902 s, 827 w, 792 s, 782 sh, 751 s, 722 sh, 650 s, *449 m*, *345 m*

It is of interest to determine the effect of this new dithiolate ligand on the ordering of these levels and to compare the result with other cobalt-dithio systems.

Fortunately, Maki, *et al.*,[13] developed the theory to make such a determination. Even though its application is quite close to that originally used, we include a brief description of the approach for completeness. Real d orbitals were chosen as a basis set and the spin-orbit interaction Hamiltonian, $\Sigma_k l_k \cdot s_k$, was applied as a first-order perturbation on the spin Hamiltonian

$$H = \beta\vec{S}g\vec{H} + \vec{I}A\vec{S}$$

where $\vec{H}$ is the magnetic field and $\vec{S}$ and $\vec{I}$ are the electron and nuclear spin operators, respectively. Depending on the ground-state configuration chosen, various sets of equations relate the g and A values to P and K. [$P = g_e g_n \beta_e \beta_n \langle r^{-3}\rangle$, where g_e and g_n are the electron and nuclear g factors, respectively, β_e and β_n are the Bohr and nuclear magnetons, respectively, and $\langle r^{-3}\rangle$ is the inverse cube electron-nuclear distance. K is the Fermi contact term.] For example, given the $(d_{xy})^2(d_{yz})^1$ ground state (using the hole formalism), the equations take the form

$$g_{xx} = 2 - 6C_1 - 2C_3 \tag{1}$$

$$g_{yy} = 2 - 2C_4 - 3C_1^2 \tag{2}$$

$$g_{zz} = 2 - 2C_2 - 3C_1^2 \tag{3}$$

$$A_{xx} = P[-6C_1 - 2C_3 - K - {}^4\!/_7 - {}^3\!/_7(C_2 + C_4) + {}^3\!/_{14}C_1^2] \tag{4}$$

$$A_{yy} = P[-2C_4 - K + {}^2\!/_7 + {}^3\!/_7(C_1 + C_2 - C_3)] \tag{5}$$

$$A_{zz} = P[-2C_2 - K + {}^2\!/_7 + {}^3\!/_7(C_3 - C_1 - C_4) - {}^9\!/_{14}C_1^2] \tag{6}$$

where C_1, C_2, C_3, and C_4 represent the effective spin-orbit coupling constant ξ_{eff} divided by the energies between the orbital containing the unpaired electron (d_{yz} here) and the d_{z^2}, d_{xz}, $d_{x^2-y^2}$, and d_{xy} orbitals.

To a first approximation, C_2 and C_3 were taken as equal to zero as was the term C_1^2. Equations 1-4 and 6 were then solved for P and K yielding preliminary values of 0.0160 cm^{-1} and 0.182 cm^{-1}, respectively. A_{yy} can then be calculated to be 0.002217 cm^{-1} compared to the experimental value of approximately 0.00278 cm^{-1}. A refinement of this calculation is possible using a nonzero value for C_2 and an estimated value for C_3

$$C_3 = C_4\left[\frac{C_4}{\alpha_1}\frac{\xi_{Cu}}{\xi_{Co}} - 1\right]^{-1}$$

where C_4 is the value found previously and ξ_{Cu} and ξ_{Co} are the free-ion spin-orbit coupling constants for cobalt(II) and copper(II), respectively. α_1 is the value for the corresponding copper system (see below). Carrying out the refined calculations yields P and K values of 0.017 cm^{-1} and 0.17 cm^{-1} which are in the proper range for cobalt(II) (see Table III). The P value is 77% of the free-ion value.[14] Recalculation of A_{yy} gives 0.002659 cm^{-1} which is much closer to the experimentally estimated value of 0.00278 cm^{-1}. All other configurations give either P or K values which are unreasonable applying the same standards of Maki, *et al.* The most probable ground state is then $(d_{xy})^2(d_{yz})^1$. Calculations based on other possible assignments of the anisotropic g values, *i.e.*, $g_{xx} = 2.279$, $g_{yy} = 1.993$, and $g_{zz} = 2.051$, were carried out.

Using the reduction of P from the free-ion value as a criterion for delocalization of electron density, the data in Table III indicate that $C_5H_4CS_2^{2-}$ and $S_2C_2(CN)_2^{2-}$ are clearly equally strong as electron-withdrawing species.

Determinations of the energy of excited-state configurations on the basis of C_1, C_2, C_3, and C_4 are not particularly accurate. Using a value of $\xi_{Co(eff)}$ of 300 cm^{-1} and $C_1 = -0.0432$, $C_3 = -0.00854$, and $C_4 = -0.0271$, energies of 6900, 35,000, and 11,000 cm^{-1} are calculated for the dif-

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(14) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **206**, 173 (1951).

Table III. P and K values for Cobalt(II)-Dithio Systems (cm^{-1})

	$Co(sacsac)_2$	$Co(mnt)_2{}^{2-}$	$Co(C_5H_4CS_2)_2{}^{2-}$
P	0.016[a]	0.020[b]	0.017
K		0.47[b]	0.17

[a] Calculated using the data in ref 15. [b] Reference 16.

ferences between the d_{yz} and the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals, respectivity. A weak band is observed at 33,500 cm^{-1} but no other peaks can be picked out of the complex ligand uv-vis peaks.

Using a spin-orbit coupling constant of 400 cm^{-1}, lowered from the free-ion value, 515 cm^{-1},[15] to the same extent as P, yields excitation energies to the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals of 9200, 46,800, and 14,800 cm^{-1}. Similar calculations for $Co(mnt)_2{}^{2-}$ give values of 3500, 46,000, and 12,400 for the corresponding transitions. Thus again, even though the geometries are different for $Co(mnt)_2{}^{2-}$ and $Co(C_5H_4CS_2)_2{}^{2-}$, it would appear that the electronic effects at the cobalt are quite similar.

While this approach to determining the ground state should be applicable to any system of D_{2h} or D_{4h} symmetry, in order to test its validity, we applied the method to the previously studied $Cu(C_5H_4CS_2)_2{}^{2-}$ system where the ground state is d_{xy} (using the coordinate system in Figure 1).

The equations become

$$g_{xx} = g_{yy} = 2 - 2\alpha_2 \tag{7}$$

$$g_{zz} = 2 - 8\alpha_1 \tag{8}$$

$$A_{xx} = A_{yy} = P[-2\alpha_2 - K + {}^2/_7 + {}^3/_7\alpha_2] \tag{9}$$

$$A_{zz} = P[-8\alpha_1 - K - {}^4/_7 - {}^3/_7(2\alpha_2)] \tag{10}$$

Solving eq 7-10 for K and P yields 0.586 and 0.0167 cm^{-1}, respectively. P is 48% of the free-ion value. The coefficient for the *d portion of the molecular orbital* was previously determined to be 0.73.[1] Normally, this value squared (0.53) is taken as the effective unpaired spin density in the d orbital. The correspondence in the lowering of the P value, an indication of covalency, and the spin density in the d portion of the molecular orbital seems quite good. While a quantitative comparison cannot be and should not be made, it would appear that these approaches to covalency do confirm the predicted effects of the ligand, that of being a strong electron acceptor in the out-of-plane fashion.

Acknowledgment. This work was supported by a grant (2385-G3) from the donors of the Petroleum Research Fund, administered by the American Chemical Society. B. J. K. thanks the Allied Chemical Corp. for financial support during the period 1972-1973.

Registry No. $Na_2C_5H_4CS_2 \cdot C_4H_8O$, 36487-17-9; $[(C_2H_5)_4N]_2Co(C_5H_4CS_2)_2$, 42230-16-0; $[(C_2H_5)_4N]_2Cd(C_5H_4CS_2)_2$, 42230-17-1.

(15) T. M. Dunn, *Trans. Faraday Soc.*, 57, 1441 (1961).

Contribution from The Procter & Gamble Company,
Miami Valley Laboratories, Cincinnati, Ohio 45239

Raman Spectral Evidence for Oxydiacetate Chelation of Alkali Metal Ions in Aqueous Solution. Interconversion among Ligand Rotational Isomers

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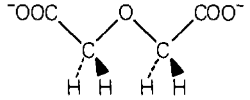
Received May 22, 1973

Raman spectra of aqueous solutions of alkali metal oxydiacetates [$O(CH_2COO)_2{}^{2-}$, ODA, with counterions Li^+, Na^+, K^+, and Cs^+] have yielded direct evidence for complexation between anion and cation. The apparent order of complex stabilities follows that of the inverse of the cation crystal radii, $Li^+ > Na^+ > K^+ > Cs^+$. This association is spectrally manifested principally in the C–C stretching region between 900 and 1000 cm^{-1}, where intensity changes result from interconversion among ODA rotational isomers. Whereas the natural (*i.e.*, unperturbed) ODA conformer distribution contains considerable nonplanar CCOCC skeletal structure, only the planar trans,trans form appears to complex alkali ions. In so doing, the trans,trans conformer functions as a tridentate chelate ligand, binding through both carboxylate groups and the ether oxygen atom. Quantitative treatment of Raman intensities suggests that the 1:1 chelate predominates in the Li^+–ODA system; presumably this also holds for the other alkali metal ions which bind ODA. The concentration formation quotient for aqueous $LiODA^-$ is calculated as 0.24 ± 0.01 M^{-1} at *ca.* 30°.

Introduction

Recently, we reported the combined use of X-ray crystallography and Raman spectroscopy to structurally characterize complexation between Ca^{2+} and the relatively simple ether-carboxylate ligand, oxydiacetate [$O(CH_2COO)_2{}^{2-}$, ODA].[1,2] By applying both techniques to examine the structure of crystalline $CaODA \cdot 6H_2O$ and then relating this structure spectroscopically to that of the 1:1 aqueous solution species, we were able to demonstrate the equivalence of the ligand's CCOCC skeletal conformation in these solid-state and solution environments (planar trans,trans,[3] shown below). A further conclusion was that in the absence of a strongly coordinating metal ion such as Ca^{2+}, ODA exists in solution as a mixture of rotational isomers having considerable nonplanar skeletal content (*i.e.*, presumably with the trans,gauche and gauche,gauche conformers predominating). Addition of Ca^{2+} to such a solution induces conformational conversion to the trans,trans form as a con-



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(1) V. A. Uchtman and R. P. Oertel, *J. Amer. Chem. Soc.*, 95, 1802 (1973).

(2) Abbreviations: oxydiacetic acid, H_2ODA; oxydiacetate dianion, ODA.

(3) The term "trans" is used here in the conformational sense; elsewhere the synonymous term "anti" may be used. Other spectroscopically distinguishable ODA skeletal conformations are trans,gauche and gauche,gauche.