Figure 1.—The $1/\chi$ vs. T diagram of several cubic uranium tungsten bronzes.

through conduction electrons.[3] Direct U–U exchange interactions must be ruled out because of the large separation between the uranium atoms (average U–U distances for each compound are presented in Table I). The possibility of superexchange in U_xWO_3 can be excluded also, since reduction of the uranium concentration and substitution of uranium by "nonmagnetic" thorium do not affect the Θ value of the system. In terms of a U–O–U superexchange model, reduction of the uranium concentration and replacement of thorium for uranium should produce a "magnetic dilution" effect. This leaves the third mechanism in which conduction electrons are assumed to provide for an exchange interaction between the uranium atoms.

That conduction electrons do, in fact, play a role in the magnetic exchange interactions of U_xWO_3 could be shown by some orienting measurements on U_xWO_3 compounds which are semiconducting rather than metallic. Uranium tungsten bronzes for $x = 0.05$, 0.03, and 0.01 exhibit paramagnetic Curie temperatures, Θ, which decrease from -85 through -65 to $-45 \pm 5°$, respectively. This indicates clearly that the conductivity of the U_xWO_3 compounds influences the exchange interaction between the uranium atoms. The effective moment of uranium in all uranium tungsten bronzes studied is $3.1 \mu_B$.

Acknowledgments.—The author wishes to thank Professor P. Hagenmuller of the University of Bordeaux, Bordeaux, France, and Dr. J. P. Williams of Corning Glass Works for stimulating discussions.

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Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

The Preparation of Ethylenediaminediacetic-N,N'-di-α-propionic Acid and the Structure of Its Cobalt(III) Complex

By Donald H. Williams, Jeanne R. Angus, and Jack Steele

It is well known that upon coordination to a metal ion like Co(III) the protons of ethylenediaminetetraacetic

acid, EDTA, become quite dissimilar. Examination with pmr techniques[1,2] reveals a difference between the in-plane and out-of-plane methylene linkages (relative to the N–Co–N plane). These results are readily rationalized with reference to the X-ray crystal structure of the Co(EDTA)$^-$ anion provided by Weakleim and Hoard.[3] The explanations put forth involve either the observation that the out-of-plane glycinates are better bonded to the Co(III) *via* the Co–O bond[4] and/or the fact that the steric situation is quite different for the out-of-plane ring.[2]

The objective of this study was, first, to compare the steric requirements at the out-of-plane site with those of the in-plane linkage. To this end a ligand has been prepared, ethylenediaminediacetic-N,N'-di-α-propionic acid, H_4EDPA, which is like EDTA except that one of the two acetate groups attached to each nitrogen atom has a methyl group in place of one of the methylene protons.[5] Also, *via* pmr analysis of the complex formed with Co(III) the possibility of steric limitation has been tested. When EDPA coordinates, there may be three geometric isomers. With optically active EDPA the number of isomers possible is 20. The notion that upon coordination to a transition metal ion a hexadentate ligand might be subject to bonding in a specific fashion is not new. Dwyer[6] demonstrated the principle dramatically with the similar hexadentate, propylenediaminetetraacetic acid, PDTA.

Experimental Section

Materials.—Ethylenediaminediacetic acid and 2-bromopropionic acid were used as obtained, the former from K & K Laboratories and the latter from Aldrich Chemicals. All other materials were of reagent grade quality.

The pmr spectra were taken on a Varian HR-60 nmr spectrometer and given in ppm relative to TMS. Visible spectra were measured on a Cary Model 15 recording spectrophotometer. Elemental analyses were obtained with the use of an F & M Model 185 gas chromatograph. The ORD measurement was made on a Cary Model 60 ORD-CD.

Ethylenediaminediacetic-N,N'-di-α-propionic Acid.—This procedure is an adaption of Dwyer's preparation of PDTA.[7] We found this method to be much less difficult and much more successful than that of Majer.[5] To 50 ml of H_2O chilled in an ice bath of 10° was added 25 ml of 2-bromopropionic acid. A solution of 24 g of NaOH in 50 ml of H_2O was added slowly so as not to allow the temperature to rise above 20°. Ethylenediaminediacetic acid (10 g) was then added. The solvent had been degassed with N_2 and an atmosphere of N_2 was maintained to minimize oxidation of the amine. The mixture was allowed to stand at room temperature (20°) for 6 days at which time it was acidified with 6.5 ml of concentrated H_2SO_4. The solution was kept at 10° for 16 hr and the Na_2SO_4 was filtered off. The EDPA was precipitated from the cooled filtrate by the addition of a mixture of 50 ml of absolute ethanol and 100 ml of acetone. The product was filtered off and washed with 5-ml portions of cold H_2O, acetone, and ether. It was recrystallized twice from minimum amounts of ethanol–H_2O mixtures (25, 75%) using acetone addition to aid precipitation; yield 4.55 g (10.1%). *Anal.* Calcd

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for Na₂H₂(C₁₂H₁₆N₂O₈)·2H₂O: C, 36.00; H, 5.50; N, 7.00.

for $Na_2H_2(C_{12}H_{16}N_2O_8)\cdot2H_2O$: C, 36.00; H, 5.50; N, 7.00. Found: C, 35.70; H, 5.45; N, 6.88. Two pmr spectra were obtained in D_2O. The product showed two doublets of equal splittings at 1.50 and 1.75 ppm in the intensity ratio of 2:1, respectively. There were singlets at 3.54 and 3.82 ppm and what appeared to be overlapping quartets centered in the 4.0-ppm region. A small amount of ligand which was obtained from two more recrystallizations had the pmr spectrum: doublet ($J = 7$ cps) centered at 1.50, a singlet at 3.54, a singlet at 3.82, and a quartet ($J = 7.5$ cps) centered at 4.03 ppm. The integration values of 3:2:2:1 confirm the assignments in ppm: doublet, CH_3; singlet at 3.5, C_2H_4; singlet at 3.8, methylenes; quartet, RCH. The ligand with the more complicated spectrum was used for complex formation.

Sodium Tris(carbonato)cobaltate(III) Trihydrate.—This compound was prepared following the method of Bauer and Drinkard.[8] The synthesis was modified to use 30 ml of H_2O_2 instead of 10 ml.

Sodium Ethylenediaminediacetate-N,N'-di-α-propionatocobaltate(III) Dihydrate.—To a solution of 4.5 g of $Na_2H_2EDPA\cdot H_2O$ in 400 ml of H_2O (at 40°) was added 4.2 g of $Na_3[Co(CO_3)_3]\cdot 3H_2O$. The solution was stirred for 4 hr and evaporated under reduced pressure to one-third volume. The solution was filtered and chilled in an ice bath. The addition of a threefold excess of ethanol to the cool solution produced violet crystals of the complex upon standing overnight at 0°; yield 1.1 g (22%). *Anal.* Calcd for $Na[Co(EDPA)]\cdot2H_2O$: C, 34.00; H, 4.74; N, 6.62. Found: C, 33.62; H, 4.96; N, 6.62. The visible spectrum has absorption maxima at 382 and 528 nm. The latter peak has a molar extinction coefficient of 332. These data compare to that for $Na[Co(EDTA)]$ with maxima at 384 and 537 nm (E_{537} 326).[9]

Results and Discussion

The pmr spectra of $Na[Co(EDTA)]$ and the new analogous complex, $Na[Co(EDPA)]$, are both shown in Figure 1 for comparison. The spectrum for the EDTA complex has been assigned elsewhere.[1,2] This seems a logical choice for comparison since the spectra of $Co(EDTA)^-$, $Co(PDTA)^-$, $Co(CyDTA)^-$, and this complex all have a basic similarity.[4] The feature of interest is the downfield AB pattern (with the lesser chemical shift difference) centered at 3.9 ppm which has been assigned to the protons of the out-of-plane methylene linkages. The out-of-plane rings are the least strained, thereby both allowing a better Co–O bond to be formed and permitting the two methylene protons to be in more similar chemical environments. The absence of this resonance in the spectrum of the EDPA complex is evidence for the specific coordination of this ligand with the propionic rings in the out-of-plane positions.

The other AB pattern centered at 3.75 ppm (with the larger chemical shift difference) has been assigned to the in-plane methylene linkage. In the EDPA complex it is shifted slightly and is more AX in nature. This latter behavior is quite reasonable since the two hydrogens lie in quite different environments, one axial, nearer the adjacent carboxyl group, and the other equatorial, crowded by the nearby methyl group.

For the complex with the dimethyl ligand the pmr spectrum reveals two doublets (both $J = 6.7$ cps) from the CH_3 at 1.5 and 1.4 ppm. This is the region expected from the data for analogous species: Co(en)-
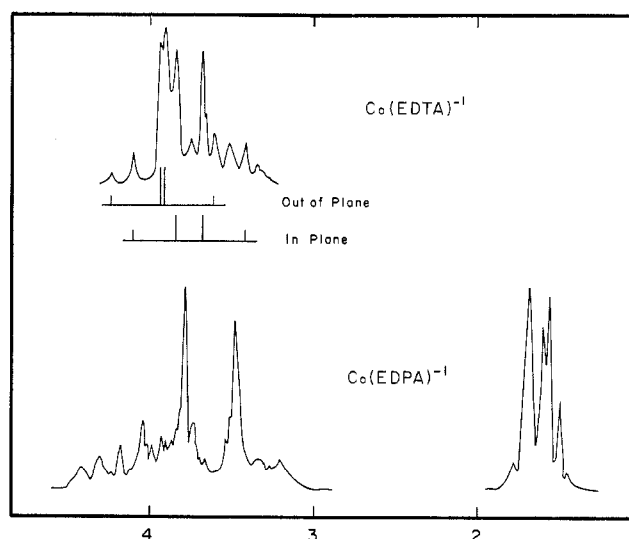

Figure 1.—Pmr, in ppm relative to TMS, of $Na[Co(EDTA)]$ and $Na[Co(EDPA)]$.

$(EDDP)^+$,[10] $Co(NH_3)_4ala^{2+}$,[11] and $K[Co(PDTA)]$.[12] The presence of two overlapping doublets (intensity ratio about 3:1) means that more than one optical form has been coordinated.[13] The other distinguishable feature is what appears to be a quartet, or overlapping quartets with a splitting of about 7 cps centered at 4.2 ppm. This pattern integrates to one-third the value of the methyl doublets.

Verification of the methyl group location as that of the out-of-plane rings comes from the fact that the spectrum of $Co(EDPA)^-$ is unchanged after the D_2O–complex solution has stood with $NaHCO_3$ for 1 week. It has been pointed out that since complexes of this sort undergo specific labilization and exchange at the out-of-plane sites, such an experiment can be used to distinguish out-of-plane from in-plane linkages.[4] The AB pattern centered at 3.6 ppm would have diminished in relative intensity if it did not represent the in-plane methylene group.

Thus, the evidence clearly demonstrates that this bulky analog to EDTA coordinates with geometric specificity, the bulkier linkages attaching to the out-of-plane sites. Work is proceeding in this laboratory to test the stereospecificity of this ligand; that is, both the ligand and its Co(III) complex are being resolved. As noted in the Experimental Section, there is nmr evidence that both *meso* and enantiomeric forms of ligand have been synthesized but only one was used in complexation. This is strongly suggested since two methyl doublets are observed.[13] If the solubilities of the various forms are like tartaric acid, then we have complexed more of the *meso* form than the enantiomers. The complex is a racemic mixture, its ORD showing only a vicinal effect. A preliminary conclusion is that

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the complex has not been formed with 100% stereo-specificity.

Correspondence

Spin–Spin Coupling in Magnetically Condensed Complexes. IX. Exchange Coupling Constants for Tetranuclear Schiff's Base Complexes of Copper(II)[1]

Sir:

Tridentate Schiff's base ligands derived from acetylacetone or salicylaldehydes and *o*-aminophenol form copper(II) complexes with unusual magnetic properties.[2] Although acetylacetonemono(*o*-hydroxyanil)copper(II) is reported to exhibit temperature-dependent magnetism which, like dimeric copper(II) acetate monohydrate, can be described by the exchange-coupled dimer equation for a singlet ground state and low-lying triplet state,[3] other similar complexes have shown complex magnetic behavior.[4] Barclay and Hoskins[5] have noted that some of these latter compounds exhibit antiferromagnetism but that there are features which are different from copper acetate. A clue to the source of the deviation is found in the description of the crystal structure of acetylacetonemono(*o*-hydroxyanil)-copper(II).[5] Although the molecule has frequently been described as a dimer, it is actually *tetrameric*. As shown schematically in Figure 1, the dimeric units are associated into pairs by coordination of bridging oxygen atoms to copper ions in adjacent molecules. The purpose of this correspondence is to show that the magnetic behavior can be described if electron spin–spin interactions among all four copper ions are taken into account. Intermolecular effects between tetramers would have to be transmitted through contacts of copper atoms 3 and 4 with carbon atoms of tetramers in adjacent unit cells. Since the Cu–C internuclear distances of 3.22 Å are on the order observed for the van der Waals forces, it is not expected that important spin–spin interactions will be transmitted through these linkages.

The arrangement of the magnetic ions presents a four-spin problem similar in essential details to the A_2X_2 problem in high-resolution nuclear magnetic resonance.[6] Four exchange coupling constants are required to describe the spin–spin interactions; these are $J_{13} = J_{24}$, $J_{23} = J_{14}$, J_{12}, and J_{34}. Although the numbering of the

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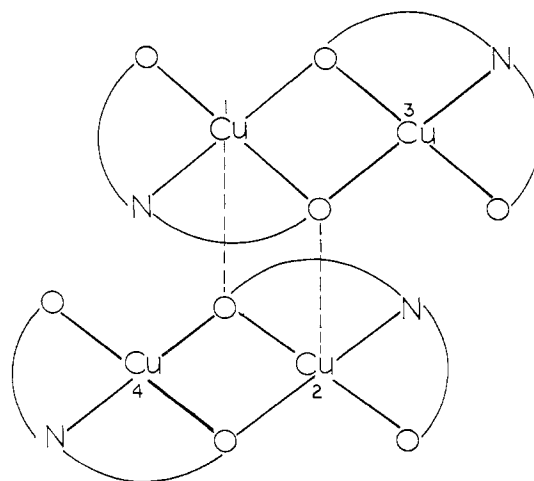

Figure 1.—A schematic representation of the structure of acetyl-acetonemono(*o*-hydroxyanil)copper(II).

copper ions in Figure 1 is arbitrary, once they are numbered it is then possible to associate a specific coupling constant with the corresponding spin–spin interaction.[7] The Hamiltonian appropriate for the problem is

$$H = -2J_{12}S_1 \cdot S_2 - 2J_{13}(S_1 \cdot S_3 + S_2 \cdot S_4) - 2J_{14}(S_1 \cdot S_4 + S_2 \cdot S_3) - 2J_{34}S_3 \cdot S_4$$

Spin wave functions and the elements of the energy matrix are given in Table I. The energy matrix factors into one 4×4 matrix, $Q(i,j)$, five 2×2 matrices, and two 1×1 matrices. While algebraic expressions in terms of the exchange coupling constants can be written for the 12 energy levels resulting from the 2×2 and 1×1 matrices, it is necessary to solve the 4×4 matrix $Q(i,j)$ in terms of choices of J parameters in order to obtain the remaining four eigenvalues.

Eigenvalues calculated for choices of the exchange coupling constants and the first-order Zeeman terms, $E_n^{(1)}$, equal to $M_s g \beta$ were substituted into the Van Vleck susceptibility expression yielding eq 1 per gram-atom of copper. The Landé g factor, temperature independent paramagnetism TIP, and the coupling constants J_{12}, J_{13}, J_{14}, and J_{34} were varied systematically, and a set of temperature-dependence-of-susceptibility curves was compiled for graphical comparison. The calculations were performed by a program written in Fortran IV for the IBM 360/75 computer of the University of North Carolina Computation Center, and the calculated and experimental curves were drawn by the Calcomp plotter.

(7) See ref 6, p 138 ff.