

nitrogen in the other. The ethyleneurea with the Hg-O bond in turn bonds to the second mercury through one of its nitrogen atoms, while the ethyleneurea, with the Hg-N bond to the first mercury, bonds through its oxygen to the second. This pattern is continued down the length of the chain. It is interesting to note that the HgCl₂ unit can cause such an ordering of amide-containing molecules when one considers that mercury taken into the body, even in the form of methylmercury salts, is converted to inorganic mercury.^{2b, 13}

The ethyleneurea groups are distorted asymmetrically as shown in Figure 3, due to bonding with two mercury atoms. The average nitrogen to carbonyl carbon distance in ethyleneurea is 1.34 Å.⁷ In this structure this carbon to nitrogen distance is lengthened when the nitrogen is in turn bonded to a mercury (C1-N2 = 1.38 ± 0.01 Å) while the other carbon to nitrogen distance not involving coordination to the mercury (N1-C1 = 1.32 ± 0.02 Å) is significantly shorter than this average. This is most easily rationalized by assuming that the electron pair on the mercury-coordinated nitrogen is involved in the coordination decreasing the electronic delocalization on that nitrogen whereas the uncoordinated nitrogen

attempts to delocalize further its nonbonding pair. The other distances and angles compare well with those found in urea and ethyleneurea.^{7, 14}

The shift in the carbonyl stretching frequency in this compound would imply Hg-N coordination exclusively, in terms of the aforementioned hypothesis. However, the coordination occurs through both the oxygen and the nitrogen with the Hg-O distance (2.67 ± 0.01 Å) shorter than the Hg-N distance (2.95 ± 0.01 Å). It is thus obvious that, in this case at least, the assignment is even qualitatively incorrect and that the reliance on a single spectral band shift as a structure indicator is inadequate to describe even a moderately complex system. Additional studies are now under way to test further the validity of this criterion in cases where the coordination involves only one type of ligand and in which the spectral shifts are of such magnitude that the prediction must stand on its own merits.

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(13) T. Norseth and T. W. Clarkson, *Biochem. Pharmacol.*, **19**, 2775 (1970).

(14) A. Caron and J. Donohue, *Acta Crystallogr., Sect. B*, **25**, 404 (1969).

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Crystal and Molecular Structure of the Dimer Complex μ -Bis[2(1H)-tetrahydropyrimidinone]-octakis[2(1H)-tetrahydropyrimidinone]-dicobalt(II) Perchlorate

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The crystal and molecular structure of the dimer complex μ -bis[2(1H)-tetrahydropyrimidinone]-octakis[2(1H)-tetrahydropyrimidinone]dicobalt(II) perchlorate, (CoC₂₀H₄₀O₁₃Cl₂)₂, has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in the space group *P* $\bar{1}$ with unit cell constants $a = 11.835 \pm 0.001$ Å, $b = 13.827 \pm 0.001$ Å, $c = 12.871 \pm 0.001$ Å, $\alpha = 101.72 \pm 0.01^\circ$, $\beta = 107.94 \pm 0.01^\circ$, and $\gamma = 117.83 \pm 0.01^\circ$. The calculated density of 1.56 g/cm³ assuming one dimer formula weight per unit cell is in agreement with the experimentally measured density of 1.55 ± 0.02 g/cm³. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to a final *R* value of 0.053 for the 1911 statistically significant reflections. Coordination occurs through the oxygen atoms with the cobalt having approximately octahedral symmetry. Each cobalt has four unique ligands and shares two others to complete the six-coordinate sphere.

Introduction

Stable complexes of metal salts with substituted ureas have been isolated for some time, but there have been many arguments in the literature about the site of coordination, either oxygen or nitrogen or both. Many references in the literature have suggested that the mode of bonding can be deduced from the position of the carbonyl stretching frequency of the complex relative to that of the free ligand.¹⁻³ A shift of the

carbonyl absorption to lower frequency is presumed to indicate oxygen to metal bonding, while a shift to higher frequency would indicate nitrogen to metal bonding. For example, based on infrared spectral data, Penland and coworkers⁴ postulated oxygen to metal bonding in urea complexes of Cr(III), Fe(III), Zn(II), and Cu(II), and nitrogen to metal bonding with Pt(II) and Pd(II). Costamagna and Levitus⁵ used similar arguments to demonstrate oxygen to

(1) B. B. Kedzia, P. X. Armendarez, and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **30**, 849 (1968).

(2) A. W. McLellan and G. A. Melson, *J. Chem. Soc. A*, 137 (1967).

(3) A. R. Katritzky and R. A. Y. Jones, *Chem. Ind. (London)*, 722 (1961).

(4) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 1575 (1957).

(5) J. A. Costamagna and R. Levitus, *J. Inorg. Nucl. Chem.*, **28**, 2685 (1966).

metal bonding in a series of cobalt complexes with N-substituted ureas. Madan and Denk⁶ correlated infrared spectra, conductance measurements, and analytical data to indicate oxygen coordination in a series of caprolactam complexes. Berni, Jonassen, and Benerito^{7,8} studied complexes of both ethyleneurea and propyleneurea with anhydrous metal chlorides. Their infrared data suggested that the 2:1 complex of ethyleneurea with cadmium chloride might be symmetrically bonded through the π cloud over the entire three-atom amide system.

A series of structural investigations has been undertaken to investigate the validity of this correlation of the shift of the carbonyl stretching frequency to the prediction of the mode of bonding. In previously reported structures, the validity of using the carbonyl stretching frequency to indicate the mode of bonding has been seriously challenged. For the cadmium ethyleneurea complex,⁹ there was no shift in the frequency but the crystal showed strong oxygen to metal bonding. In a mercury(II) chloride complex also with ethyleneurea,¹⁰ the shift would have predicted nitrogen to metal bonding, but the structure showed strong oxygen to metal bonding and only weak nitrogen to metal bonding. The structure reported herein was undertaken to discern its coordination sphere since it showed a shift indicative of oxygen to metal bonding. If it does indeed show oxygen to metal bonding, then there must be some alternate reason for the large shift in the carbonyl frequency that was not present in the cadmium complex.

Experimental Section

Suitable single crystals for an X-ray study were kindly provided by A. G. Pierce of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Dept. of Agriculture in New Orleans, La. A single irregularly shaped crystal with a maximum dimension of 0.2 mm was mounted with the (0 \bar{k} 0) axis coincident with the ϕ axis of a General Electric XRD-5 diffractometer. The reciprocal lattice showed no evidence of mirror or rotation symmetry nor any systematic absences, limiting the crystal to a triclinic system and either space group $P1$ or $P\bar{1}$. Lattice constants for a primitive unit cell were then determined by a least-squares fit of 29 carefully measured 2θ values of the Cu $K\alpha_1$ and Cu $K\alpha_2$ doublet for $2\theta > 75^\circ$ under fine conditions (1° takeoff angle and 0.05° slit). The resultant lattice constants and their estimated standard deviations are $a = 11.835 \pm 0.001 \text{ \AA}$, $b = 13.827 \pm 0.001 \text{ \AA}$, $c = 12.871 \pm 0.001 \text{ \AA}$, $\alpha = 101.72 \pm 0.01^\circ$, $\beta = 107.94 \pm 0.01^\circ$, and $\gamma = 117.83 \pm 0.01^\circ$.

The experimental density of 1.55 g/cm^3 (measured by a flotation technique) agrees with the calculated density of 1.56 g/cm^3 for one dimer unit per unit cell with formula $(\text{Co}(\text{pu})_2)^{2+}(\text{ClO}_4)_2^{2-}$, where pu is propyleneurea (or 2(1*H*)-tetrahydropropyrimidinone).

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using balanced Zr and Y filters and molybdenum $K\alpha$ radiation. A total of 1911 reflections were considered observed¹¹ from the measured 4541 reflections to a 2θ

(6) S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, **27**, 1049 (1965).

(7) R. J. Berni, R. R. Benerito, W. M. Ayres, and H. B. Jonassen, *ibid.*, **25**, 807 (1963).

(8) R. J. Berni, R. R. Benerito, and H. B. Jonassen, *ibid.*, **31**, 1023 (1969).

(9) J. N. Brown, A. G. Pierce, Jr., and L. M. Trefonas, *Inorg. Chem.*, **11**, 1830 (1972).

(10) R. J. Majeste and L. M. Trefonas, *ibid.*, **11**, 1834 (1972).

(11) A listing of the values of the observed and calculated structure factors has been deposited as Document No. 1760 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. 20540. A copy may be secured by citing the document number and by remitting \$5.00 for photoprints or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

limit of 50° using the criterion $(I_{Zr} - 2\sigma(I_{Zr})) - (I_Y + 2\sigma(I_Y)) > 75$ counts, where the σ 's are based on counting statistics for a counting time of 10 sec. Lorentz-polarization corrections were made in the usual manner and absorption (normalized transmission factors range from 1.0–1.21) was corrected as a function of ϕ only (linear absorption coefficient $\mu = 8.0 \text{ cm}^{-1}$ for Mo radiation). Primary and secondary extinction effects were extremely small and hence corrections for these effects were not made.

Structure Determination

A three-dimensional Patterson function was calculated and used to resolve the ambiguity between $P1$ and $P\bar{1}$. A set of Co and Cl vectors was found which was consistent with the space group $P\bar{1}$ and hence all subsequent refinements were limited to that space group. The coordinates and isotropic temperature factors of the cobalt and two chlorine atoms¹² were refined by block-diagonal least squares to a value of $R = 0.37$. An electron density map phased by these atoms revealed 23 of the missing 43 atoms. Isotropic refinements, using $1/\sigma^2$ weights, for these 26 atoms led to $R = 0.28$. A second electron density map was then calculated and the remainder of the nonhydrogen atoms were located. Isotropic refinement of all 46 nonhydrogen atoms led to $R = 0.10$. After conversion to anisotropic temperature factors, refinement was continued until convergence at $R = 0.059$.

A difference electron density map was then calculated to locate the hydrogen coordinates. Positive regions of electron density were found at most of the anticipated hydrogen positions but not at all of them. Therefore, the hydrogen atom coordinates were calculated, based upon expected geometry (CH–NH distance 1.0 \AA), and included in subsequent structure factor calculations but not refined. Refinement was continued for the nonhydrogen atoms until the shifts were less than one-tenth the estimated standard deviations of the respective parameters. The final $R = 0.053$.

Results and Discussion

Table I lists the final coordinates and anisotropic temperature factors for all nonhydrogen atoms together with the estimated standard deviations (esd's) for all parameters. Table II lists the calculated hydrogen coordinates. Figure 1 illustrates the coordination about the cobalt cation with bond distances and bond angles given. In all cases the Co–O bond distances have esd's less than 0.002 \AA and the O–Co–O angles have esd's less than 0.1° . Figure 2 shows the average distances and angles within the five unique propyleneurea moieties. The esd's for distances and angles within each propyleneurea are less than 0.008 \AA and 0.6° , respectively. Table III lists the distances and angles within the perchlorate groups. Again, the esd's are less than 0.005 \AA and 0.4° .

The perchlorate group is usually assumed¹³ to have tetrahedral symmetry with Cl–O distances in the range 1.40 – 1.48 \AA . Unfortunately, it is also usually found to be disordered in crystallographic studies¹⁴ and depending on the manner in which the disordering is handled, a much wider variation is observed in the Cl–O distances combined with a similar variation in the O–Cl–O angles. In this study the perchlorate group refines as an ordered group although with somewhat increased temperature factors indicating disordering to at least a small extent. The Cl–O distances range from 1.32 to 1.43 \AA with an average distance of 1.39 \AA . The O–Cl–O angles range from 107

(12) The scattering factors of all nonhydrogen atoms were from D. Cromer and J. Waber, *Acta Crystallogr.*, **18**, 104 (1965), and those for hydrogen were from R. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). The weighted square of the residuals $r = w|k|F_o| - |F_c||^2$ was minimized with the conventional reliability index (R) cited throughout the paper.

(13) B. Dickens, *Acta Crystallogr., Sect. B*, **25**, 404 (1969).

(14) A. Camerman and L. H. Jensen, *ibid.*, **25**, 2623 (1969).

TABLE I
FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS^a

| Atom | X | Y | Z | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|------|------------|-------------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Co | 0.3996 (0) | 0.0464 (0) | 0.0259 (0) | 51 (0) | 47 (0) | 44 (0) | 27 (0) | 18 (0) | 13 (0) |
| C11 | 0.2057 (1) | 0.4090 (1) | 0.0944 (1) | 132 (1) | 97 (1) | 107 (1) | 71 (1) | 44 (1) | 47 (1) |
| Ox1 | 0.0583 (3) | 0.3274 (3) | 0.0600 (3) | 146 (4) | 193 (4) | 268 (5) | 91 (4) | 71 (4) | 93 (4) |
| Ox2 | 0.2584 (3) | 0.3446 (3) | 0.0504 (2) | 258 (5) | 189 (4) | 136 (3) | 166 (4) | 76 (3) | 43 (3) |
| Ox3 | 0.2163 (4) | 0.4932 (3) | 0.0481 (3) | 355 (7) | 172 (4) | 214 (5) | 144 (4) | 99 (5) | 134 (4) |
| Ox4 | 0.2860 (3) | 0.4655 (3) | 0.2195 (2) | 316 (6) | 221 (4) | 109 (3) | 188 (4) | 66 (4) | 53 (3) |
| C12 | 0.9024 (1) | 0.1928 (1) | 0.5278 (1) | 163 (1) | 110 (1) | 91 (1) | 88 (1) | 27 (1) | 23 (1) |
| Ox5 | 0.7862 (3) | 0.1938 (3) | 0.4606 (3) | 208 (5) | 336 (6) | 296 (6) | 199 (5) | 101 (5) | 214 (5) |
| Ox6 | 0.9644 (4) | 0.1776 (4) | 0.4556 (3) | 407 (8) | 322 (6) | 259 (5) | 285 (6) | 208 (6) | 133 (5) |
| Ox7 | 0.8462 (5) | 0.0914 (3) | 0.5546 (3) | 579 (11) | 231 (5) | 265 (6) | 255 (6) | 213 (7) | 192 (5) |
| Ox8 | 0.9952 (4) | 0.2891 (3) | 0.6296 (3) | 387 (8) | 211 (5) | 210 (5) | 112 (6) | -12 (5) | -106 (4) |
| O1 | 0.6132 (2) | 0.1143 (1) | 0.0524 (2) | 54 (2) | 43 (2) | 76 (2) | 18 (2) | 16 (2) | 1 (1) |
| C11 | 0.7219 (3) | 0.2194 (2) | 0.1239 (2) | 83 (4) | 67 (3) | 63 (3) | 52 (3) | 26 (3) | 27 (2) |
| N21 | 0.7446 (3) | 0.3136 (2) | 0.1010 (2) | 127 (4) | 60 (2) | 64 (3) | 40 (3) | 23 (3) | 22 (2) |
| C31 | 0.8634 (4) | 0.4363 (3) | 0.1822 (3) | 203 (6) | 49 (3) | 93 (4) | 19 (4) | 30 (4) | 31 (3) |
| C41 | 0.9517 (6) | 0.4440 (4) | 0.2852 (5) | 283 (10) | 64 (4) | 286 (9) | -3 (5) | -147 (7) | 8 (5) |
| C51 | 0.9455 (4) | 0.3539 (3) | 0.3151 (3) | 146 (6) | 106 (4) | 96 (4) | 28 (4) | -22 (4) | 8 (3) |
| N61 | 0.8179 (3) | 0.2374 (2) | 0.2264 (2) | 112 (4) | 70 (3) | 71 (3) | 35 (3) | 13 (3) | 26 (2) |
| O2 | 0.4440 (2) | 0.2163 (2) | 0.1186 (2) | 120 (3) | 65 (2) | 57 (2) | 52 (2) | 31 (2) | 13 (2) |
| C12 | 0.5069 (3) | 0.2873 (2) | 0.2270 (2) | 78 (4) | 36 (2) | 65 (3) | 22 (3) | 38 (3) | 15 (2) |
| N22 | 0.5078 (3) | 0.3857 (2) | 0.2576 (2) | 179 (5) | 66 (2) | 59 (3) | 68 (3) | 39 (3) | 16 (2) |
| C32 | 0.5648 (4) | 0.4652 (3) | 0.3811 (3) | 263 (8) | 83 (4) | 104 (4) | 98 (5) | 47 (5) | -7 (3) |
| C42 | 0.6395 (6) | 0.4418 (5) | 0.4613 (3) | 490 (13) | 337 (9) | 63 (4) | 352 (10) | -48 (6) | -56 (5) |
| C52 | 0.6463 (4) | 0.3463 (3) | 0.4407 (3) | 226 (7) | 127 (4) | 67 (4) | 101 (5) | 32 (4) | 33 (3) |
| N62 | 0.5769 (3) | 0.2688 (2) | 0.3149 (2) | 169 (4) | 100 (3) | 59 (3) | 92 (3) | 32 (3) | 20 (2) |
| O3 | 0.4525 (2) | 0.0295 (2) | 0.1841 (2) | 106 (3) | 70 (2) | 78 (2) | 45 (2) | 40 (2) | 34 (2) |
| C13 | 0.3995 (3) | -0.0551 (2) | 0.2151 (2) | 88 (4) | 77 (3) | 65 (3) | 54 (3) | 51 (3) | 33 (2) |
| N23 | 0.4815 (3) | -0.0495 (2) | 0.3200 (2) | 109 (4) | 95 (3) | 84 (3) | 31 (3) | 28 (3) | 48 (2) |
| C33 | 0.4337 (4) | -0.1389 (3) | 0.3650 (3) | 183 (6) | 134 (4) | 110 (4) | 64 (4) | 57 (4) | 99 (4) |
| C43 | 0.3213 (5) | -0.2535 (3) | 0.2690 (4) | 255 (8) | 102 (4) | 142 (5) | 78 (5) | 55 (5) | 73 (4) |
| C53 | 0.2027 (4) | -0.2546 (3) | 0.1800 (3) | 127 (5) | 98 (4) | 107 (4) | 32 (4) | 40 (4) | 39 (3) |
| N63 | 0.2665 (3) | -0.1530 (2) | 0.1475 (2) | 95 (4) | 84 (3) | 84 (3) | 45 (3) | 28 (3) | 31 (2) |
| O4 | 0.3392 (2) | 0.0548 (2) | 0.8623 (2) | 112 (3) | 71 (2) | 64 (2) | 59 (2) | 39 (2) | 36 (2) |
| C14 | 0.3390 (3) | 0.1328 (2) | 0.8271 (3) | 71 (4) | 68 (3) | 73 (3) | 36 (3) | 53 (3) | 29 (2) |
| N24 | 0.4104 (3) | 0.2477 (2) | 0.9029 (2) | 149 (4) | 61 (2) | 80 (3) | 38 (3) | 42 (3) | 30 (2) |
| C34 | 0.3937 (5) | 0.3318 (4) | 0.8604 (4) | 356 (10) | 130 (5) | 209 (6) | 167 (6) | 209 (7) | 98 (5) |
| C44 | 0.3056 (7) | 0.2926 (5) | 0.7436 (6) | 418 (13) | 150 (6) | 309 (10) | 84 (8) | -89 (9) | 138 (7) |
| C54 | 0.2483 (4) | 0.1804 (4) | 0.6575 (3) | 267 (8) | 192 (6) | 118 (4) | 170 (6) | 99 (5) | 111 (4) |
| N64 | 0.2676 (3) | 0.1013 (2) | 0.7094 (2) | 190 (5) | 104 (3) | 61 (2) | 105 (3) | 41 (3) | 41 (2) |
| O5 | 0.8172 (2) | 0.0464 (2) | 0.0154 (2) | 70 (3) | 113 (2) | 93 (2) | 54 (2) | 37 (2) | 54 (2) |
| C15 | 0.9144 (3) | 0.0456 (3) | 0.0910 (3) | 51 (4) | 94 (3) | 87 (3) | 38 (3) | 35 (3) | 33 (3) |
| N25 | 0.9031 (2) | -0.0546 (2) | 0.0874 (2) | 96 (3) | 74 (2) | 93 (3) | 48 (2) | 46 (3) | 42 (2) |
| C35 | 1.0150 (4) | -0.0569 (3) | 0.1748 (3) | 150 (6) | 166 (5) | 166 (5) | 130 (5) | 105 (5) | 109 (4) |
| C45 | 1.1342 (6) | 0.0573 (5) | 0.2580 (5) | 325 (11) | 208 (7) | 228 (7) | 170 (8) | -165 (7) | -2 (6) |
| C55 | 1.1543 (4) | 0.1619 (4) | 0.2632 (4) | 102 (5) | 169 (6) | 175 (6) | 60 (5) | -12 (4) | 53 (5) |
| N65 | 1.0339 (3) | 0.1494 (2) | 0.1739 (3) | 107 (4) | 91 (3) | 120 (3) | 43 (3) | 18 (3) | 36 (3) |

^a Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Anisotropic thermal parameters $\times 10^4$; estimated standard deviations in parentheses refer to the last decimal place.

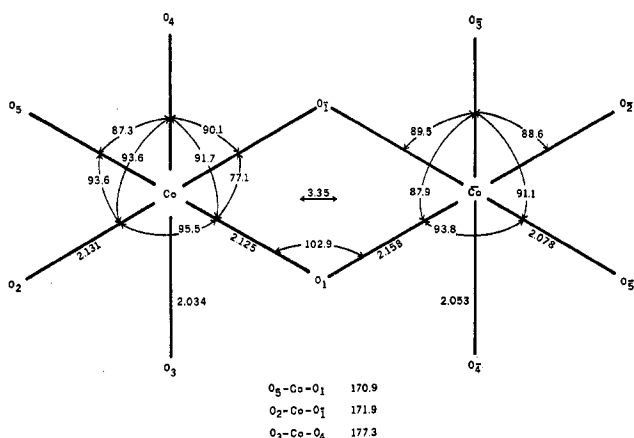


Figure 1.—Schematic drawing of the coordination sphere about the cobalt

to 113° with an average angle of 109° . The oxygens exhibit several contact distances less than 3.25 \AA which accounts for the relatively fixed perchlorate group observed in this study.

TABLE II
CALCULATED HYDROGEN COORDINATES^a

| Atom ^b | X | Y | Z | Atom ^b | X | Y | Z |
|-------------------|-------|--------|-------|-------------------|-------|--------|-------|
| H21 | 0.672 | 0.298 | 0.020 | H43' | 0.369 | -0.278 | 0.223 |
| H31 | 0.824 | 0.486 | 0.200 | H53 | 0.142 | -0.248 | 0.221 |
| H31' | 0.923 | 0.474 | 0.140 | H53' | 0.135 | -0.335 | 0.108 |
| H41 | 0.947 | 0.496 | 0.353 | H63 | 0.204 | -0.158 | 0.068 |
| H41' | 1.055 | 0.498 | 0.298 | H24 | 0.472 | 0.275 | 0.992 |
| H51 | 0.947 | 0.367 | 0.398 | H34 | 0.495 | 0.398 | 0.874 |
| H51' | 1.036 | 0.357 | 0.326 | H34' | 0.370 | 0.376 | 0.913 |
| H61 | 0.798 | 0.162 | 0.242 | H44 | 0.346 | 0.367 | 0.714 |
| H22 | 0.466 | 0.406 | 0.190 | H44' | 0.212 | 0.288 | 0.743 |
| H32 | 0.479 | 0.455 | 0.395 | H54 | 0.305 | 0.200 | 0.608 |
| H32' | 0.624 | 0.552 | 0.392 | H54' | 0.145 | 0.142 | 0.600 |
| H42 | 0.613 | 0.450 | 0.529 | H64 | 0.223 | 0.016 | 0.653 |
| H42' | 0.746 | 0.514 | 0.497 | H25 | 0.813 | -0.134 | 0.019 |
| H52 | 0.595 | 0.296 | 0.482 | H35 | 1.048 | -0.100 | 0.133 |
| H52' | 0.750 | 0.372 | 0.481 | H35' | 0.972 | -0.104 | 0.220 |
| H62 | 0.585 | 0.198 | 0.292 | H45 | 1.222 | 0.063 | 0.256 |
| H23 | 0.585 | 0.024 | 0.369 | H45' | 1.145 | 0.060 | 0.342 |
| H33 | 0.393 | -0.119 | 0.421 | H55 | 1.245 | 0.211 | 0.253 |
| H33' | 0.517 | -0.140 | 0.418 | H55' | 1.177 | 0.212 | 0.346 |
| H43 | 0.282 | -0.317 | 0.300 | H65 | 1.042 | 0.226 | 0.174 |

^a Isotropic temperature factor fixed at 4.0 \AA^2 . ^b Numbers refer to bonding atom.

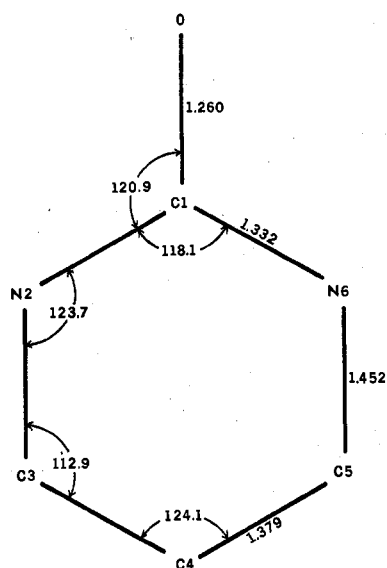


Figure 2.—Schematic drawing of the molecule with the average bond distances and angles within the propyleneurea groups indicated.

TABLE III
INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)
WITHIN THE PERCHLORATE GROUPS^a

| | | | |
|---------|-------|-------------|-------|
| C11-Ox1 | 1.414 | Ox4-C11-Ox3 | 110.2 |
| C11-Ox2 | 1.427 | Ox4-C11-Ox2 | 107.8 |
| C11-Ox3 | 1.385 | Ox4-C11-Ox1 | 110.1 |
| C11-Ox4 | 1.400 | Ox3-C11-Ox2 | 112.2 |
| | | Ox3-C11-Ox1 | 107.5 |
| | | Ox2-C11-Ox1 | 109.1 |
| C12-Ox5 | 1.389 | Ox8-C12-Ox7 | 108.2 |
| C12-Ox6 | 1.391 | Ox8-C12-Ox6 | 113.0 |
| C12-Ox7 | 1.414 | Ox8-C12-Ox5 | 112.5 |
| C12-Ox8 | 1.317 | Ox7-C12-Ox6 | 108.3 |
| | | Ox7-C12-Ox5 | 107.1 |
| | | Ox6-C12-Ox5 | 107.5 |

^a Esd's for distances and angles are less than 0.005 Å and 0.3°, respectively.

The propyleneurea groups are internally consistent and have expected molecular parameters. The carbon-oxygen and carbon-nitrogen average bond distances of 1.26 and 1.33 Å, respectively, compare favorably to those cited by Donohue¹⁵ (1.270, 1.32 Å) and by Post¹⁶ (1.262, 1.341 Å) for urea. Likewise, the bond angles are also similar. The drawing, Figure 3, does indicate crystal packing disordering at the C4 position of each propyleneurea group. This disordering was apparent from the initial least squares refinements and persisted throughout a variety of attempts to situate these atoms in a way which both compensated for it and was simultaneously chemically reasonable. The N2's and N6's had normal isotropic temperature factors of about 4 Å², C3's and C5's were about 5 Å², and the C4's were approximately 6 Å². The large average angle C3-C4-C5, 124°, and the short C3-C4 and average C5-C4 average distances, 1.38 Å, are attributed to this orientational disordering.

Each of the propyleneurea groups is planar in the amide region (O, C1, N2, and N6) to within 0.007 Å as determined by a best least-squares plane fit of the atoms. In general, as more carbons are added (C3

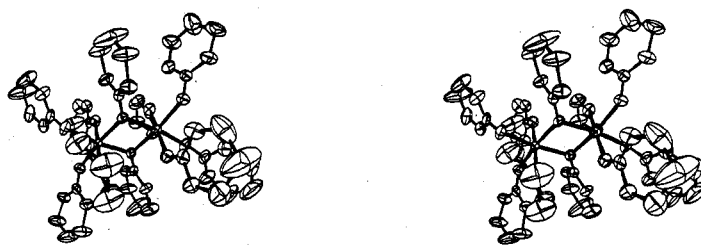


Figure 3.—ORTEP diagram of the cation.

and C5 and then C4) the planarity decreases to 0.05 Å except for ring 3 which is 0.16 Å. In actuality, ring 4 is the least disordered of the propyleneurea groups and conforms to the expected nonplanarity when C4 is added to the calculation.

The primary interest in the structure was the coordination sphere about the cobalt rather than the ligands and the perchlorate groups. The molecule exists as a dimer complex with each cobalt having a slightly distorted octahedral coordination sphere as shown in Figure 1. There are four unique ligands per cobalt, each coordinating through the oxygen, and two bridging ligands in which the oxygens are shared by two cobalt atoms. The Co-O distances differ enough from each other, even when grouped as apical or bridging, that no attempt has been made to cite average values for either category. The two oxygens in apical positions, O3 and O4, relative to the plane defined by Co, Co, O1, and O1, have the shortest Co-O distances of 2.034 and 2.053 Å, respectively, whereas Co-O2 and Co-O3 are 2.131 and 2.078 Å, respectively. The Co-O distances involved in the bridge are 2.125 and 2.158 Å. This variation in coordination distances can be attributed to the difficulty in packing the propyleneurea moieties about the cobalt as can be seen in the ORTEP drawing.

The molecule exhibits both inter- and intramolecular contact distances characteristic of hydrogen bonding but does not possess the strong hydrogen bonding found in the cadmium-ethyleneurea complex previously studied.⁹ There are three probable intermolecular bonds (distance of dotted bonds given in parentheses): N23-H23...Ox5 (2.12 Å; ∠NHO 169°), N64-H64...Ox6 (2.25 Å; ∠NHO 152°), and N65-H65...Ox1 (2.21 Å; ∠NHO 139°); and three probable intramolecular bonds: N62-H62...Ox3 (1.93 Å; ∠NHO 135°), N63-H63...Ox5 (2.12 Å; ∠NHO 140°), and N24-H24...Ox2 (2.01 Å; ∠NHO 136°). These closest contacts along with the other close contacts in the unit cell are illustrated in Figure 4.

In this particular compound the carbonyl stretching frequency is shifted -52 and -63 cm⁻¹ from that of free propyleneurea itself. This shift and the oxygen to metal coordination conform to the spectral predictions. However, the cadmium complex⁹ showed no shift but had oxygen coordination, and the mercury complex¹⁰ which shifted to higher frequency indicative of nitrogen coordination was found to involve primarily oxygen to metal coordination. The use of frequency shifts of so-called characteristic bands in the infrared absorption spectrum of a compound to indicate the mode of coordination is an extremely poor and unre-

(15) A. Caron and J. Donohue, *Acta Crystallogr., Sect. B*, **25**, 404 (1969).

(16) N. Sklar, M. E. Senko, and B. Post, *ibid.*, **14**, 716 (1961).

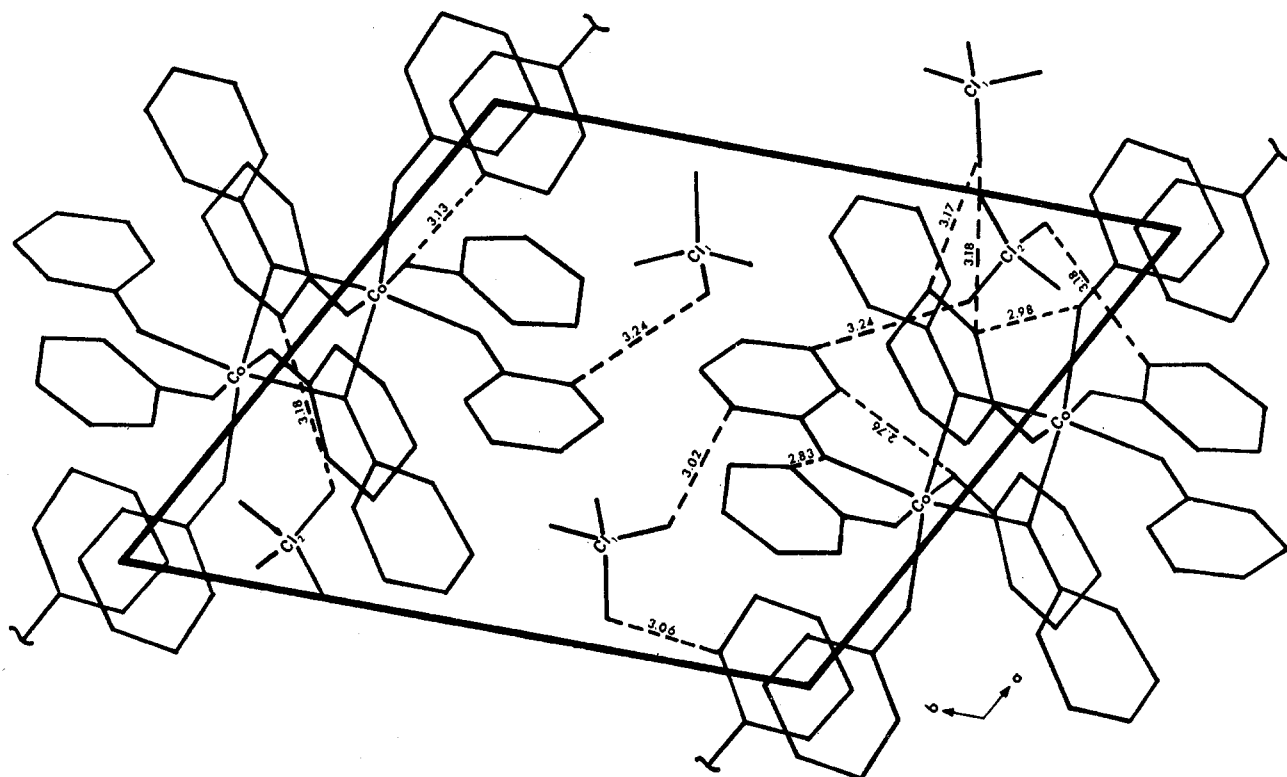


Figure 4.—Projection of the unit cell contents down the (00*l*) axis showing hydrogen-bonding scheme.

liable tool. Actually, the best prediction of bonding sites in substituted ureas is to assume that metal to oxygen bonds are the primary factor in the coordination.

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CONTRIBUTION FROM THE MATERIALS SCIENCE DIVISION,
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A Neutron Diffraction Study of Monoaquotetraureadioxouranium(VI) Nitrate¹

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The crystal structure of $\{\text{UO}_2(\text{H}_2\text{O})[\text{CO}(\text{NH}_2)_2]_4\}(\text{NO}_3)_2$ has been determined by neutron diffraction. The compound is monoclinic with $a = 9.99$ (2), $b = 14.99$ (3), $c = 13.18$ (3) Å, $\beta = 100.08$ (3)°, and space group $P2_1/c$ with $Z = 4$. Preliminary X-ray data were used to locate the approximate positions of the uranium and nonhydrogen atoms of the urea and water ligands, utilizing the heavy atom method. The atoms of the nitrate ions and hydrogen atoms were located and a least-squares refinement completed using neutron data to an $R_w = 4.7\%$. The uranyl ion is nearly linear with a U—O distance of 1.77 (2) Å and is surrounded by a planar pentagon consisting of five oxygen atoms, four from urea ligands at distances of 2.34 (1)–2.38 (1) Å and one from the water ligand at a distance of 2.46 (2) Å. The plane formed by these oxygen atoms is nearly perpendicular to the axis of the O—U—O ion. The structure is connected by an extensive system of hydrogen bonds which involve nitrate ions both through coordination and through bridging *via* hydrogen bonds.

Introduction

The coordination of the uranyl ion in $\text{UO}_2(\text{H}_2\text{O})\text{[CO}(\text{NH}_2)_2\text{]}_4(\text{NO}_3)_2$ has been a matter of some disagreement. Campisi,² on the basis of infrared results, postulated that the compound should be formulated

as $\{\text{UO}_2(\text{H}_2\text{O})[\text{CO}(\text{NH}_2)_2]_4(\text{NO}_3)\}\text{NO}_3$ with the uranyl ion surrounded by six oxygen atoms—four from urea ligands, one from a water ligand, and one from a monodentate nitrate group. Gentile³ proposed a polymeric structure with a sixfold coordination about the uranyl consisting of four oxygen atoms from urea ligands, an

(1) Research supported by the U. S. Atomic Energy Commission.

(2) L. S. Campisi, Ph.D. Dissertation, Fordham University, New York, N. Y., 1965.

(3) P. S. Gentile, Fordham University, private communication.