between those of the Cp and Bz ligands, although more closely akin to the former, and behaves in a manner consistent with the predictions of the ligand field approach.

Registry No. $Cr(C_5H_5BH)_2$, 68344-21-8; $Mn(C_5H_5BH)_2$, 68344-22-9; $Fe(C_5H_5BH)_2$, 68344-23-0; $Co(C_5H_5BH)_2$, 68378-62-1; $Fe(C_5H_5BCH_3)_2$, 54853-80-4; $Co(C_5H_5BCH_3)_2$, 36534-27-7.

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Notes

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Structure of Pentakis(urea)dioxouranium(VI) Nitrate, $[UO_2(OC(NH_2)_2)_5](NO_3)_2$[1]

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In our ongoing studies of uranium complexes we have determined the crystal structure of $UO_2(OC(NH_2)_2)_5(NO_3)_2$ by X-ray diffraction. Gentile and Campisi[2] reported the preparation of this compound and concluded, on the basis of infrared spectra, that the nitrate groups are not coordinated to uranium, a fact which we confirm. The uranyl ion is coordinated by oxygen atoms of the five urea molecules in a complex which is monomeric, not a polymer as suggested earlier.[2]

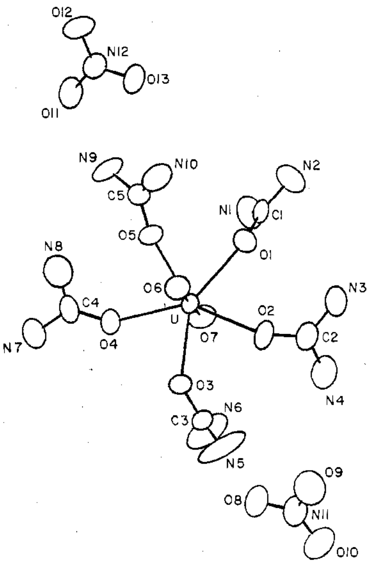

Figure 1. ORTEP view of $[UO_2(OC(NH_2)_2)_5][NO_3]_2$ showing the numbering scheme.

Experimental Section

From an aqueous solution of uranyl nitrate and urea which was allowed to evaporate slowly overnight, small fluorescent lime green crystals precipitated. The crystals were stable in air and showed no decomposition during the 2 weeks the X-ray experiments were being conducted. Weissenberg photography showed the crystal to be monoclinic, and rough cell dimensions were obtained.

A crystal of dimensions 0.08 × 0.11 × 0.21 mm was glued to a glass fiber and examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of the 800, 040, and 006 reflections showed peaks with half-widths of 0.16, 0.15, and 0.11°, respectively. The setting angles of eight manually centered reflections ($16° < 2\theta < 25°$) using Mo Kβ (λ 0.632 288 Å) and three reflections ($40° < 2\theta < 43°$) using Mo Kα_1 were used to determine the cell parameters $a = 15.944$ (8) Å, $b = 8.952$ (4) Å, $c = 15.394$ (6) Å, $\beta = 106.31$ (3)°, and $V = 2108.8$ Å^3. The observed extinctions are unique to space group $P2_1/n$. For $Z = 4$ and a molecular weight of 694.32 the calculated density is 2.19 g cm^{-3}.

Intensity data were collected with a scan speed of 2°/min on 2θ. Each reflection was scanned from 0.7° before the Kα_1 peak to 0.7° after the Kα_2 peak, and backgrounds were counted for 4 s at each end of the scan range. The temperature during data collection was 21 ± 1 °C. Three standard reflections were measured after every 200th scan. The 10 524 scans, not including standards, resulted in 4869 unique intensities, 2954 of which were greater than 3σ. An absorption correction was applied,[3] $\mu = 73$ cm^{-1}, and the maximum and minimum corrections were 2.24 and 1.77, respectively. The intensities of all three standards decayed about 3% during the data collection period, and the data were corrected accordingly.

The trial coordinates of the uranium atom position were derived from a three-dimensional Patterson function. The Fourier map, calculated with the phases of the uranium atom alone, revealed 11 of the light atoms. A least-squares refinement and the subsequent Fourier calculation, phased by the 12 atoms, revealed the locations of the remaining atoms. A series of least-squares refinements in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized coverged rapidly to the final structure. The expressions that were used in processing the data and estimating the weights are available as supplementary material; the "ignorance factor", p, was set to 0.03. Scattering factors from Doyle and Turner[4] were used, and anomalous dispersion corrections[5] (for U, $f' = -10.673$ and $f'' = 9.654$) were applied. Hydrogen atoms could not be identified in the final difference maps and were not included in the least-squares refinement. The largest peak in the last difference Fourier map was 1.2 e. Anisotropic thermal

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Table I. Postional Parameters with Estimated Standard Deviations[a] for $[UO_2(OC(NH_2)_2)_5][NO_3]_2$

atom	x	y	z
U	0.10526 (2)	0.23262 (3)	0.35415 (2)
O(1)	0.2351 (3)	0.2567 (6)	0.4749 (3)
O(2)	0.2221 (3)	0.1642 (7)	0.2981 (4)
O(3)	0.0470 (3)	0.1537 (6)	0.2019 (3)
O(4)	−0.0473 (3)	0.2691 (7)	0.3158 (4)
O(5)	0.0692 (3)	0.3429 (6)	0.4807 (3)
O(6)	0.0933 (3)	0.0518 (6)	0.3944 (4)
O(7)	0.1176 (4)	0.4166 (6)	0.3192 (4)
O(8)	0.6173 (4)	0.0050 (7)	0.4578 (4)
O(9)	0.7213 (5)	0.1643 (8)	0.4926 (5)
O(10)	0.7080 (5)	0.0237 (8)	0.3782 (5)
O(11)	0.0014 (4)	0.2446 (8)	0.7611 (4)
O(12)	0.0511 (4)	0.1518 (7)	0.8930 (4)
O(13)	0.1235 (4)	0.1202 (7)	0.7956 (4)
N(1)	0.2544 (5)	0.5006 (8)	0.5172 (5)
N(2)	0.3484 (5)	0.3197 (9)	0.5930 (5)
N(3)	0.3676 (5)	0.1744 (9)	0.3638 (5)
N(4)	0.3080 (5)	0.2755 (9)	0.2204 (6)
N(5)	0.0893 (8)	0.078 (1)	0.0839 (6)
N(6)	0.0677 (7)	0.322 (1)	0.1021 (7)
N(7)	0.8104 (5)	0.306 (1)	0.2907 (6)
N(8)	0.8867 (5)	0.175 (1)	0.4180 (6)
N(9)	0.0250 (5)	0.3883 (8)	0.6045 (4)
N(10)	0.1122 (5)	0.1836 (8)	0.6007 (5)
N(11)	0.6821 (5)	0.0652 (8)	0.4426 (6)
N(12)	0.0592 (5)	0.1723 (8)	0.8174 (5)
C(1)	0.2775 (5)	0.359 (1)	0.5269 (5)
C(2)	0.2976 (5)	0.205 (1)	0.2940 (6)
C(3)	0.0671 (5)	0.184 (1)	0.1312 (5)
C(4)	0.8860 (5)	0.243 (1)	0.3415 (6)
C(5)	0.0691 (5)	0.3060 (9)	0.5612 (5)

[a] Here and in the following tables the numbers in parentheses are the estimated standard deviations in the least significant digit.

parameters were included for all atoms refined. The discrepancy indices for 2954 data where $I > 3\sigma$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.032$$

R for all 4869 data is 0.073. The error in an observation of unit weight is 1.09. In the last cycle no parameter changed more than 0.11σ.

A powder pattern, calculated from this structure and listed in the supplementary material, is consistent with the pattern published by Gentile and Campisi.[2]

Results and Discussion

Atomic parameters, distances, and angles are listed in Tables I–III. The molecular structure (Figure 1) consists of a uranium atom at the center of a pentagonal bipyramid of two uranyl oxygen atoms at each apex and of five urea oxygen atoms on the equator. The average U–O(urea) distance is 2.38 Å (corrected for thermal motion). The uranium atom and the equatorial atoms are all within 0.09 Å of their least-squares plane which is nearly perpendicular to the O–U–O axis. The geometry and bond distances and angles are in very close agreement with those found by a neutron diffraction study[6] in $UO_2(H_2O)(OC(NH_2)_2)_4(NO_3)_2$, in which water occupies one of the coordination sites. In both structures the nitrate and urea groups are planar, and nitrate ions have no close contacts to uranium.

Hydrogen bonding in the structure is mostly rather weak. There are only five N(urea)–O(nitrate or urea) distances that are less than 3 Å and only one of these is less than 2.9 Å; see Table II. As in the tetrakis(urea) compound, there are numerous other N–O contacts in the range 3.0–3.3 Å which may be very weak hydrogen bonds, but there is no satisfactory way to assign all of the hydrogen atoms to them. There are no N(urea)–O(uranyl) short distances.

Table II. Interatomic Distances (Å)

atoms	distance	corr[a] distance
	Uranium Neighbors	
U-O(6)	1.76 (1)	1.78
-O(7)	1.76 (1)	1.78
-O(1)	2.37 (1)	2.38
-O(2)	2.34 (1)	2.36
-O(3)	2.37 (1)	2.38
-O(4)	2.36 (1)	2.38
-O(5)	2.39 (1)	2.40
	Urea	
C(1)-O(1)	1.28 (1)	1.28
C(2)-O(2)	1.28 (1)	1.29
C(3)-O(3)	1.25 (1)	1.25
C(4)-O(4)	1.26 (1)	1.26
C(5)-O(5)	1.28 (1)	1.28
C(1)-N(1)	1.32 (1)	1.35
-N(2)	1.34 (1)	1.37
C(2)-N(3)	1.34 (1)	1.36
-N(4)	1.35 (1)	1.37
C(3)-N(5)	1.30 (1)	1.39
-N(6)	1.32 (1)	1.39
C(4)-N(7)	1.36 (1)	1.36
-N(8)	1.32 (1)	1.41
C(5)-N(9)	1.32 (1)	1.35
-N(10)	1.34 (1)	1.37
	Nitrate	
N(11)-O(8)	1.25 (1)	1.26
-O(9)	1.22 (1)	1.26
-O(10)	1.23 (1)	1.27
N(12)-O(11)	1.25 (1)	1.30
-O(12)	1.22 (1)	1.25
-O(13)	1.25 (1)	1.28
	Possible H Bonds (under 3 Å)	
N(4)-O(11)	2.98 (1)	
N(5)-O(12)	2.91 (1)	
N(6)-O(8)	2.99 (1)	
N(9)-O(5)	2.94 (1)	
N(9)-O(11)	2.85 (1)	

[a] Corrected for thermal motion assuming the "riding" model.

Table III. Selected Angles (deg)

O(6)-U-O(7)	177.3 (3)	N(1)-C(1)-N(2)	119.0 (8)
O(1)-U-O(2)	72.8 (2)	N(3)-C(2)-N(4)	119.6 (8)
O(2)-U-O(3)	71.9 (2)	N(5)-C(3)-N(6)	117.9 (9)
O(3)-U-O(4)	72.8 (2)	N(7)-C(4)-N(8)	119.0 (9)
O(4)-U-O(5)	71.3 (2)	N(9)-C(5)-N(10)	119.9 (8)
O(5)-U-O(1)	71.4 (2)	O(1)-C(1)-N(1)	122.4 (8)
O(6)-U-O(1)	88.1 (2)	O(10)-C(1)-N(2)	118.6 (8)
O(6)-U-O(2)	93.7 (2)	O(2)-C(2)-N(3)	119.0 (9)
O(6)-U-O(3)	91.3 (2)	O(2)-C(2)-N(4)	121.4 (9)
O(6)-U-O(4)	90.5 (2)	O(3)-C(3)-N(5)	120.6 (10)
O(6)-U-O(5)	91.1 (2)	O(3)-C(3)-N(6)	121.6 (9)
O(7)-U-O(1)	90.4 (2)	O(4)-C(4)-N(7)	116.0 (10)
O(7)-U-O(2)	88.0 (3)	O(4)-C(4)-N(8)	124.7 (8)
O(7)-U-O(3)	91.3 (2)	O(5)-C(5)-N(9)	119.4 (8)
O(7)-U-O(4)	89.4 (3)	O(5)-C(5)-N(10)	120.7 (8)
O(7)-U-O(5)	86.3 (2)	O(8)-N(11)-O(9)	120.0 (8)
C(1)-O(1)-U	138.6 (6)	O(8)-N(11)-O(10)	120.2 (9)
C(2)-O(2)-U	143.1 (6)	O(9)-N(11)-O(10)	119.8 (8)
C(3)-O(3)-U	132.3 (6)	O(11)-N(12)-O(12)	118.9 (7)
C(4)-O(4)-U	143.3 (6)	O(11)-N(12)-O(13)	120.3 (7)
C(5)-O(5)-U	138.1 (6)	O(12)-N(12)-O(13)	120.8 (7)

Registry No. $UO_2(OC(NH_2)_2)_5(NO_3)_2$, 17871-18-0.

Supplementary Material Available: Data processing fomulas, a table of anisotropic thermal parameters, the calculated powder pattern, and the listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Nature of the Copper(I) Carbonyl Formed by Acid Cuprous Chloride in the Presence of Carbon Monoxide

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Acid solutions of cuprous chloride have long been used to absorb carbon monoxide,[1] but in spite of a history of over 125 years the exact nature of the copper complex or complexes formed *in solution*[2] when CO is absorbed has never been satisfactorily determined. Among the formulas proposed are a cation[3a] $Cu(CO)^+$, an anion[3b], a carbonyl halide[3c] Cu(CO)Cl, and the dimer[3d] $Cu_2(CO)Cl_2$.

During the investigation of methods for increasing the efficiency of the CO/O_2 fuel cell,[4] the interaction of CO with a series of solutions containing Cu(I) in hydrochloric acid was investigated by several electrochemical techniques. Some of the potentiometric measurements resulting from this study have been interpreted so as to define the most probable formula of the species formed in acid cuprous chloride when CO is absorbed.

Experimental Section

Copper(I) chloride was purchased as reagent grade (Mallinckrodt) and repurified according to standard procedures.[5] Nitrogen, carbon dioxide, and carbon monoxide (Matheson) were passed through a heated copper catalyst (BASF) at 120 °C (N_2 and CO_2) or 40 °C (CO) to remove traces of oxygen. Just prior to use, each gas was bubbled through aqueous HCl of the same concentration as the Cu(I) solution under study to saturate the gas with water vapor and HCl. All other chemicals were purchased as reagent grade and used as received.

The cell consisted of a three-necked, 500-mL, round-bottomed flask. A platinum wire indicator electrode and a Beckman saturated calomel reference electrode (SCE) were sealed into the cell through the two side necks. A gas inlet–outlet system, equipped with stopcocks and a fritted-glass bubbler, was sealed through the center neck.

Copper(I) solutions were prepared by the following procedure. Concentrated (37%) hydrochloric acid and distilled water were mixed in the cell. Oxygen was removed by freezing the solution with liquid nitrogen, evacuating the cell on a vacuum line, and then filling the cell with nitrogen gas. The desired amount of copper(I) chloride was then added to the solution under a positive pressure of nitrogen, the cell was resealed, and gases were again removed by vacuum pumping. Small amounts of oxygen were inevitably introduced during the addition of the copper(I) chloride but were found to be necessary in order to produce a small but sufficient Cu(II) concentration for stable potentiometric readings. The solution was stirred rapidly, and the potential of the cell was monitored using a Leeds and Northrup potentiometer until the readings became stable (30–60 min). These solutions are colorless or pale yellow if small amounts of Cu(II) are present. No solids were observed prior to or during the addition of carbon monoxide.

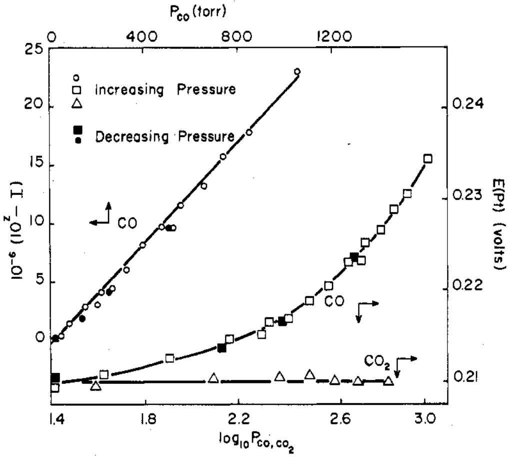

Figure 1. The nonlinear relationship between measured cell potential, *E*(Pt), and the logarithm of the equilibrium partial pressure of carbon monoxide, P_{CO}, contrasted with the linear relationship obtained from eq 11 assuming one carbonyl per complex. The potential of the cell is reversibly altered by the presence of carbon monoxide but is insensitive to the presence of carbon dioxide.

In a typical run nitrogen was first introduced into the cell to establish a baseline potential in the absence of carbon monoxide and check that the inlet system had been cleared of oxygen. Gases were then evacuated as before, and the background pressure (water vapor, residual nitrogen, and HCl vapor) was measured using a manometer attached to the gas outlet side of the cell. Carbon monoxide was introduced (2–5 Torr increase/min) until the desired reading on the manometer had been reached. The solution was stirred rapidly until no further drop in pressure or change in potential could be observed (typically 2–4 h). Final pressure and cell potential were noted, and more carbon monoxide was introduced.

A baseline potential (no CO present) was also measured on a copper indicator electrode prior to the start of each run. The copper electrode was removed prior to the addition of carbon monoxide.

The introduction of oxygen into the cell during a run caused a large (100–200 mV) jump in the cell potential which was irreversible when the gas was removed from the cell. At the end of each run the CO pressure was reduced to determine whether the potential readings at low CO pressures could be reestablished.

Each solution was analyzed for total copper both by standard iodometric procedures[6] and by atomic absorption. Total chloride was determined by the Volhard method.[7]

Results and Discussion

Well-established potentiometric methods exist for obtaining metal:ligand ratios in reactions involving complex formation.[8] In this specific case the cell potential measured on the Pt indicator electrode, *E*(Pt), vs. a saturated calomel electrode will vary with the partial pressure of CO over the solution because the formation of a copper(I) carbonyl complex alters a_{Cu^+}, the Cu^+ ion activity, by an amount related to the magnitude of the stability constant for the carbonyl.

$$E(\mathrm{Pt}) = E°_{\mathrm{Cu^{2+},Cu^+}} - E(\mathrm{SCE}) + 0.059 \log (a_{\mathrm{Cu^{2+}}}/a_{\mathrm{Cu^+}}) \quad (1)$$

$E°_{Cu^{2+},Cu^+}$, the standard electrode potential for the Cu^{2+},Cu^+ couple vs. the normal hydrogen electrode (NHE),[9] *E*(SCE), the saturated calomel reference potential vs. NHE,[10] and $a_{Cu^{2+}}$, the activity of the Cu^{2+} ion in solution, are constant. Numerical values for both a_{Cu^+} and $a_{Cu^{2+}}$ can be determined by combining eq 1 with eq 2 where *E*(Cu) is the cell potential

$$E(\mathrm{Cu}) = E°_{\mathrm{Cu^+,Cu^0}} - E(\mathrm{SCE}) + 0.059 \log a_{\mathrm{Cu^+}} \quad (2)$$

measured on a copper indicator electrode and $E°_{Cu^+,Cu^0}$ is the standard electrode potential of the Cu^+,Cu^0 couple vs. NHE.[11]

Any valid potentiometric treatment is expected to yield a Cu:CO ratio of 1:1 for the complex or complexes in question because a limit of one CO molecule per Cu atom is approached but never exceeded during gas absorption.[1,12] If only *one* single carbonyl complex is formed which is significantly more stable than all other Cu(I) complexes present in solution, a plot of the cell potential vs. the log of the partial pressure of CO should be linear with a slope of 0.059 for this ratio.[8] As shown in Figure 1 the plot is not even linear.

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