2350 *Inorg. Chem.* **1986**, *25*, 2350–2354

Contribution from the Department of Chemistry,
Technion-Israel Institute of Technology, Haifa 32000, Israel

Crystal Structures of (Glycinamido)- and (Glycinato)tetraammineruthenium(III) Chelates. Effects of the Metal Center Electronic Configuration on Coordinated Amido and Carboxylato Groups

Yigal Ilan* and Moshe Kapon

Received December 3, 1985

The crystal structures of two tetraammineruthenium(III) chelates—with glycine and with glycinamide—have been determined by X-ray structure analysis. The glycinamido chelate structure is $P\bar{1}$, with a = 11.309 Å, b = 8.990 Å, c = 7.890 Å, α = 91.79°, β = 90.52°, γ = 105.85°, and Z = 2. The glycinato chelate structure is also $P\bar{1}$, with a = 10.996 Å, b = 9.039 Å, c = 7.929 Å, α = 92.21°, β = 92.86°, γ = 106.70°, and Z = 2. The crystalline compounds are both isomorphous and isostructural. The cations are octahedral with some distortion due to constraints imposed by the chelate rings, which are considerably nonplanar. The metal–amido nitrogen bond in the glycinamido chelate is ~0.16 Å shorter than the metal–amino (and –ammonia) nitrogen bonds. This difference is significantly larger than in analogous Co(III) chelates. The C–O and C–N bonds in the Ru(III)-coordinated amido group are similar in length to the corresponding bonds in free amides, contrary to the situation in Co(III) analogues. The difference between the two C–O bond lengths of Ru(III)-coordinated carboxylate is larger than the corresponding difference in Co(III) analogues. These phenomena are discussed in terms of a ligand to metal π interaction and are compared to similar results in square-planar chelates of peptides with d^8 (Cu(III), Ni(II), Pd(II), Pt(II)) and d^9 (Cu(II)) transition-metal ions.

Introduction

Complexes of the substitution inert center Co(III) with amino acids, peptides, and their derivatives have contributed much to improve our understanding of the interaction between metal ions and biological molecules.[1] More recently, similar complexes of the substitution inert metal center Ru(III) have been prepared and studied.[2-5] Ru(III) is much more effective than Co(III) in promoting hydrolysis of both esters[3] and amides[4] of glycine at acidic pH.

The interaction between ammineruthenium(III) groups and constituents of proteins—amino acids and their derivatives—is also relevant to recent studies in which the $Ru(NH_3)_5$ group has been attached to various proteins in order to study electron-transfer reactions between ruthenium ions and metal centers of metalloproteins[6,7] and as a probe of various effects on the structure of proteins.[8]

In former studies, tetraammineruthenium and pentaammineruthenium complexes of glycine, glycinamide, and their derivatives were prepared and characterized spectroscopically and electrochemically, and their thermodynamic stabilities and chemical reactivities have been studied.[2-5] This paper presents the results of a structural analysis of two ruthenium(III) chelates: the N,N′-bound (glycinamido)tetraammineruthenium(III) chelate (I, X = NH, in Figure 1) and the N,O-bound (glycinato)tetraammineruthenium(III) chelate (II, X = O, in Figure 1).

Table I. X-ray Crystallographic Data and Other Structure Refinement Details of (Glycinamido)tetraammineruthenium(III) Hexafluorophosphate (I) and of (Glycinato)tetraammineruthenium(III) Hexafluorophosphate (II)

	compd I	compd II
empirical formula	$C_2H_{17}ON_6RuP_2F_{12}$	$C_2H_{16}O_2N_5RuP_2F_{12}$
fw	532.17	533.16
cryst size, mm	0.15 × 0.15 × 0.3	0.10 × 0.15 × 0.3
$F(000)$	522	522
a, Å	11.309 (4)	10.996 (4)
b, Å	8.990 (3)	9.039 (3)
c, Å	7.890 (3)	7.929 (3)
α, deg	91.79 (5)	92.21 (5)
β, deg	90.52 (5)	92.86 (5)
γ, deg	105.85 (5)	106.70 (5)
V, Å^3	771.2	752.8
Z	2	2
space group	$P\bar{1}$	$P\bar{1}$
D_{calcd}, g cm^{-3}	2.293	2.353
μ(Mo Kα), cm^{-1}	13.96	14.20
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan speed, ω deg min^{-1}	3	3
scan width, ω deg	1.10	1.10
angular range (in 2θ), deg	5–50	5–50
bkgd at each side of peak	10	10
monitor reflcns	211; $\bar{3}0\bar{1}$; 004	$\bar{1}\bar{1}1$; 111; $2\bar{1}1$
criterion for including reflcns	$F_o > 1.5\sigma(F_o)$	$F_o > 1.5\sigma(F_o)$
no. of unique reflcns	2707	2641
no. of reflcns at the final refinement stage	2572	2458
no. of refined params	295	281
R^a	0.043	0.038
$R_w{}^b$	0.051	0.037
weighting scheme (w)	$1/(\sigma^2(F_o) + 0.0044(F_o)^2)$	$1.79/\sigma^2(F_o)$

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \sum w^{1/2}||F_o| - |F_c||/w^{1/2}\sum|F_o|$.

When the crystallographic results for these Ru(III) chelates and results for analogous Co(III) chelates[9-11] are compared, the effect of the electronic configuration of the metal centers (Co(III), d^6; Ru(III), d^5; both low spin) on the M–L bond lengths, as well

---

(1) Buckingham, D. A. In *Biological Aspects of Inorganic Chemistry*; Addison, A. W., Cullen, W. R., Dolphin, D., James, R. R., Eds.; Wiley: New York, 1977; pp 141–196.

(2) (a) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1655–1664. (b) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 3144–3151.

(3) Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4725–4729.

(4) Ilan, Y.; Kfir, A., to be submitted for publication.

(5) (a) Yeh, A.; Taube, H. *Inorg. Chem.* **1980**, *19*, 3740–3742. (b) Scott, N.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3135–3138.

(6) Crutchley, R. J.; Ellis, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 5002–5004 and references therein.

(7) (a) Isied, S. S.; Kuehn, C.; Worosila, G. *J. Am. Chem. Soc.* **1984**, *106*, 1722–1726. (b) Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443–517 and references therein.

(8) Recchia, J.; Matthews, C. R.; Rhee, M. J.; Horrocks, W. D., Jr. *Biochim. Biophys. Acta* **1982**, *702*, 105–111 and references therein.

(9) Barnet, M. T.; Freeman, H. C.; Buckingham, D. A.; Hsu, I.-N.; van der Helm, D. *J. Chem. Soc., Chem. Commun.* **1970**, 367–368.

(10) Evans, E. J.; Hawkins, C. J.; Rodgers, J.; Snow, M. R. *Inorg. Chem.* **1983**, *22*, 34–38. Two amide groups are bound to the metal ion in this case, and the crystallographic results are complicated by the fact that two independent molecules are present in the cell and the molecular geometry is affected by packing forces. The values presented in the tables for this chelate are mean values of the four amido groups (Table VI) or of the two carboxylato groups (Table VII) present in a cell unit.

(11) (a) Anderson, B. F.; Bell, J. D.; Buckingham, D. A.; Cresswell, P. J.; Gainsford, G. J.; Marzilli, L. G. *Inorg. Chem.* **1977**, *16*, 3233–3244. (b) Buckingham, D. A.; Dwyer, M.; Gainsford, G. J.; Ho, J. V.; Marzilli, L. G.; Robinson, W. T.; Sargeson, A. M.; Turnball, K. R. *Inorg. Chem.* **1975**, *14*, 1739–1752. (c) Buckingham, D. A.; Cresswell, P. J.; Dellaca, R. J.; Dwyer, M.; Gainsford, G. J.; Marzilli, L. G.; Maxwell, I. E.; Robinson, W. T.; Sargeson, A. M.; Turnball, K. R. *J. Am. Chem. Soc.* **1974**, *96*, 1713–1725.

0020-1669/86/1325-2350$01.50/0

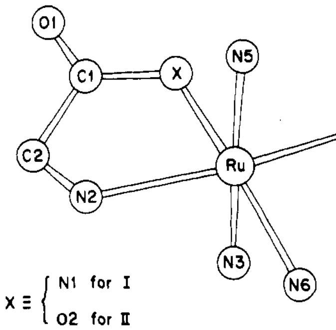

Figure 1. Structural formula and labeling diagram for (glycinamido)tetraammineruthenium(III) (X = NH) and (glycinato)tetraammineruthenium(III) (X = O) cations.

as on the bond lengths within the coordinated amido and carboxylato groups, is revealed. The bond length variations are discussed in relation to the electronic interaction between the metal center and the ligand and to electronic resonance within the amido and carboxylato groups.

Experimental Section

Chemicals and Reagents. $[(NH_3)_5RuCl]Cl_2$ was prepared from ruthenium trichloride (Johnson Matthey Chemicals) by the method of Ferguson and Love[12] and was purified by recrystallization from 0.1 M HCl. *cis*-$[(NH_3)_4Ru(H_2O)_2](CF_3SO_3)_3$ was prepared from $[(NH_3)_5RuCl]Cl_2$ by converting it to the cis oxalato complex and dissolving this in 6 M CF_3SO_3H, as described by Diamond.[13]

Glycine (Merck) and glycinamide (Aldrich Chemical Co.) were used without further purification. All other chemicals were reagent grade and were used without further purification. Deionized water that was distilled twice in an all-glass apparatus was used throughout.

I and II were prepared as the PF_6^- salts, as described before.[2a] The powders were dissolved in a minimal volume of a 0.01 M CF_3SO_3H, 0.1 M NH_4PF_6 solution, filtered off, and left in a desiccator over NaOH. After 3–5 days, the crystals were filtered off and washed with absolute ethanol and diethyl ether Crystals of I were obtained as yellow prismatic needles, and those of II as colorless prisms.

Intensity Measurements and Structure Solution. Single crystals of both compounds were mounted on a Philips PW 1100 four-circle diffractometer, and accurate cell parameters were obtained from 25 carefully centered reflections. These and other pertinent measurement details are presented in Table I. Intensities were corrected for Lp but not for absorption and converted to lists of structure factors.

The structures of I and II were solved by the heavy-atom method. Patterson syntheses revealed the position of the Ru atom, whereas the light atoms and the PF_6^- ions were located from difference Fourier maps. All calculations were carried out by the SHELX 77 program package.[14] In structure I, one of the PF_6^- ions was found in two different major and minor orientations due to disorder of the fluorine octahedra around the common phosphorus atom. The best position of the ion with the minor orientation has been obtained by allowing an ideal octahedron of fluorines to orient as a rigid body around the fixed phosphorus atom. The structure was then allowed to refine anisotropically with respect to all non-hydrogen atoms of the complex cation, one PF_6^- ion with full occupancy and another with a partial occupancy of 0.8. The ion with the minor orientation was refined isotropically with occupancy of 0.2. As for structure II, all non-hydrogen atoms were refined anisotropically in the conventional way. Hydrogens of the complex cation were located in both structures from difference Fourier maps at the final refinement stages, and their coordinates were allowed to shift isotropically. However, one of the N(6) hydrogens in structure II was refined less accurately. Unit weights were introduced at the initial stages and statistical weights at the late stages of the structure refinement. After convergence was reached, electron density excursions no higher than 0.7 e Å^{-3} were found in the vicinity of the PF_6^- ions.

Tables IIa and IIIa present the final coordinates and equivalent temperature factors, and Tables IIb and IIIb (suplementary material) present the anisotropic temperature factors for the two chelates. Bond lengths and angles are presented in Tables IV and V for compounds I and II respectively. Lists of structure factors and anisotropic thermal parameters are deposited as supplementary material.

Table IIa. Final Fractional Coordinates and Equivalent Temperature Factors[a] for (Glycinamido)tetraammineruthenium(III) Hexafluorophosphate[b]

atom	x	y	z	U_{eq}/U_{iso}, Å^2
Ru	24230 (3)	15574 (4)	22428 (4)	189 (1)
C(1)	44 (5)	−523 (6)	2812 (7)	27 (1)
C(2)	889 (5)	−1352 (6)	3579 (8)	31 (1)
O(1)	−1092 (4)	−1065 (5)	2820 (6)	36 (1)
N(1)	621 (4)	795 (5)	2091 (6)	27 (1)
N(2)	2138 (4)	−293 (6)	3927 (6)	27 (1)
N(3)	2317 (6)	3097 (7)	4279 (7)	33 (1)
N(4)	2460 (6)	3318 (6)	493 (7)	37 (1)
N(5)	2600 (5)	65 (6)	181 (6)	31 (1)
N(6)	4405 (5)	2283 (7)	2483 (7)	34 (1)
P(1)	4693 (1)	7391 (2)	2625 (2)	286 (3)
F(1)	4679 (4)	6093 (5)	3938 (5)	54 (1)
F(2)	4836 (4)	6235 (5)	1095 (5)	58 (1)
F(3)	3246 (4)	6823 (6)	2383 (5)	59 (1)
F(4)	4750 (4)	8723 (5)	1272 (6)	57 (1)
F(5)	4549 (5)	8556 (5)	4116 (6)	61 (1)
F(6)	6149 (4)	7979 (6)	2836 (6)	61 (1)
P(2)	8443 (2)	3838 (2)	2458 (3)	537 (6)
F(7)[c]	9058 (6)	5580 (5)	2116 (12)	81 (3)
F(8)	7859 (12)	2064 (7)	2753 (10)	134 (6)
F(9)	8464 (8)	4137 (8)	4480 (7)	75 (2)
F(10)	7127 (6)	4196 (13)	2382 (17)	110 (3)
F(11)	8274 (13)	3512 (8)	530 (7)	112 (4)
F(12)	9749 (11)	3516 (13)	2564 (11)	138 (4)
F(7)′	8116	4387	4282	261 (32)
F(8)′	8774	3297	620	54 (34)
F(9)′	9793	3913	3111	50 (4)
F(10)′	7977	2083	2965	64 (30)
F(11)′	7102	3772	1775	148 (47)
F(12)′	8911	5596	1923	153 (43)
HC(21)	62 (6)	−168 (7)	423 (8)	2 (1)
HC(22)	103 (6)	−222 (8)	294 (8)	4 (2)
HN(1)	46 (13)	185 (16)	133 (16)	18 (5)
HN(21)	262 (8)	−70 (10)	403 (10)	4 (2)
HN(22)	211 (10)	−61 (13)	564 (14)	12 (4)
HN(31)	169 (9)	229 (11)	536 (11)	9 (3)
HN(32)	205 (6)	360 (9)	414 (9)	5 (2)
HN(33)	307 (15)	357 (17)	460 (17)	0 (6)
HN(41)	156 (13)	349 (15)	75 (15)	13 (5)
HN(42)	336 (15)	371 (16)	5 (18)	16 (5)
HN(43)	224 (11)	301 (13)	−66 (15)	9 (4)
HN(51)	197 (8)	−3 (9)	−33 (10)	5 (2)
HN(52)	234 (14)	−65 (16)	17 (16)	10 (5)
HN(53)	332 (14)	1 (15)	−7 (16)	17 (5)
HN(61)	478 (8)	183 (10)	269 (10)	14 (3)
HN(62)	460 (7)	304 (10)	323 (10)	12 (2)
HN(63)	479 (7)	253 (10)	117 (10)	15 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i \cdot a_j)$. [b] Coordinates for Ru are ×10^5, for the remaining non-hydrogen atoms ×10^4, and for the hydrogens ×10^3. U_{eq} values for Ru and P are ×10^4 and for the remaining non-hydrogen atoms ×10^3. U_{iso} values for hydrogens are ×10^2. Esd's are in parentheses. [c] Atoms F(7)–F(12) and F(7)′–F(12)′ are with occupancies of 0.8 and 0.2, respectively.

Structure Description

The two crystalline compounds are both isomorphous and isostructural. The labeling diagram of the cations is shown in Figure 1, where site X is occupied by either a nitrogen atom of an amido group or an oxygen of a carboxylato group. The amido nitrogen in I is negatively charged and carries only one hydrogen, whereas in II, the carboxylate oxygen is also charged but lacks a hydrogen. These differences between the ligands are not large enough to alter the packing of the various ions. Moreover, structure I is found less ordered than II, as one of the PF_6^- ions takes up two distinct orientations, but this does not affect the overall arrangement.

Stereoscopic views of the two complex cations are shown in Figure 2. The geometry is rather similar in both structures (Tables IV and V). The octahedral configuration around the ruthenium is somewhat distorted due to the geometrical constraints

---

(12) Ferguson, J. E.; Love, J. L. *Inorg. Synth.* **1971**, *13*, 208–212.
(13) Diamond, S. E. Ph.D. Thesis, Stanford University, 1975.
(14) Sheldrick, G. M. "SHELX 77. Program for Crystal Structure Determination"; University of Cambridge, Cambridge England, 1977.

Table IIIa. Final Fractional Coordinates and Equivalent Temperature Factors for (Glycinato)tetraammineruthenium(III) Hexafluorophosphate[a]

atom	x	y	z	U_{eq}/U_{iso}, Å^2
Ru	23987 (4)	15437 (4)	21824 (5)	193 (1)
C(1)	48 (4)	−569 (6)	2912 (6)	251 (11)
C(2)	1004 (5)	−1290 (6)	3729 (8)	323 (13)
O(1)	−1088 (3)	−1125 (4)	3041 (5)	365 (9)
O(2)	511 (3)	641 (4)	2060 (4)	267 (8)
N(2)	2292 (4)	−154 (5)	3955 (6)	267 (10)
N(3)	2264 (5)	3118 (6)	4135 (7)	326 (12)
N(4)	2220 (6)	3164 (7)	409 (7)	390 (13)
N(5)	2438 (6)	−18 (7)	163 (7)	342 (13)
N(6)	4408 (6)	2433 (9)	2341 (9)	390 (16)
P(1)	4729 (1)	7368 (2)	2619 (2)	274 (3)
F(1)	4768 (4)	6101 (4)	3949 (4)	546 (10)
F(2)	4698 (4)	6154 (4)	1110 (4)	589 (11)
F(3)	3229 (3)	6850 (6)	2553 (5)	689 (14)
F(4)	4707 (4)	8635 (5)	1273 (5)	602 (11)
F(5)	4766 (4)	8588 (5)	4128 (5)	660 (12)
F(6)	6239 (3)	7905 (5)	2696 (5)	611 (11)
P(2)	8346 (2)	3871 (2)	2545 (2)	363 (3)
F(7)	9200 (4)	5572 (4)	2301 (6)	684 (13)
F(8)	7477 (5)	2163 (5)	2795 (6)	784 (15)
F(9)	8477 (5)	4173 (5)	4531 (5)	717 (14)
F(10)	7120 (4)	4495 (5)	2481 (6)	752 (14)
F(11)	8188 (5)	3559 (5)	565 (5)	799 (16)
F(12)	9557 (5)	3280 (6)	2640 (6)	823 (15)
HC(21)	77 (6)	−166 (7)	487 (8)	6 (2)
HC(22)	108 (5)	−210 (7)	311 (7)	3 (2)
HN(21)	242 (4)	25 (6)	510 (6)	2 (1)
HN(22)	275 (6)	−59 (7)	394 (8)	5 (2)
HN(31)	181 (6)	365 (7)	390 (7)	3 (2)
HN(32)	293 (8)	373 (9)	443 (10)	4 (3)
HN(33)	218 (7)	276 (9)	507 (10)	6 (3)
HN(41)	212 (7)	277 (9)	−56 (10)	6 (3)
HN(42)	140 (8)	331 (8)	64 (9)	7 (2)
HN(43)	260 (8)	406 (10)	67 (10)	6 (3)
HN(51)	229 (12)	−78 (14)	47 (15)	16 (5)
HN(52)	226 (11)	14 (13)	−83 (16)	14 (5)
HN(53)	303 (13)	0 (16)	−16 (19)	12 (7)
HN(61)	474 (8)	268 (10)	186 (9)	10 (3)
HN(62)	366 (6)	266 (7)	290 (8)	19 (2)
HN(63)	474 (9)	185 (11)	276 (12)	10 (4)

[a] Coordinates for Ru are ×10^5, for the remaining non-hydrogen atoms ×10^4, and for the hydrogens ×10^3. U_{eq} values for the non-hydrogen atoms are ×10^4 and U_{iso} values for the hydrogens are ×10^2. Esd's are in parentheses.

Table IV. Important Bond Lengths (Å) and Angles (deg) for (Glycinamido)tetraammineruthenium(III) Hexafluorophosphate[a]

Ru–N(1)	1.966 (4)	Ru–N(6)	2.161 (5)
Ru–N(2)	2.119 (4)	C(1)–C(2)	1.497 (9)
Ru–N(3)	2.113 (5)	C(1)–O(1)	1.244 (6)
Ru–N(4)	2.125 (5)	C(1)–N(1)	1.334 (6)
Ru–N(5)	2.122 (5)	C(2)–N(2)	1.489 (6)
N(1)–Ru–N(2)	80.4 (2)	N(3)–Ru–N(6)	89.5 (2)
N(1)–Ru–N(3)	91.1 (2)	N(4)–Ru–N(5)	88.9 (2)
N(1)–Ru–N(4)	92.3 (2)	N(4)–Ru–N(6)	90.8 (2)
N(1)–Ru–N(5)	91.0 (2)	N(5)–Ru–N(6)	88.4 (2)
N(1)–Ru–N(6)	176.9 (2)	N(1)–Ru–N(2)	80.4 (2)
N(2)–Ru–N(3)	90.4 (2)	C(2)–C(1)–O(1)	121.7 (5)
N(2)–Ru–N(4)	172.6 (2)	C(2)–C(1)–N(1)	114.1 (5)
N(2)–Ru–N(5)	90.7 (1)	O(1)–C(1)–N(1)	124.2 (4)
N(2)–Ru–N(6)	96.6 (2)	C(1)–C(2)–N(2)	111.7 (4)
N(3)–Ru–N(4)	90.2 (2)	Ru–N(1)–C(1)	119.9 (3)
N(3)–Ru–N(5)	177.8 (2)	Ru–N(2)–C(2)	108.3 (3)

[a] Esd's are in parentheses.

Table V. Important Bond Lengths (Å) and Angles (deg) for (Glycinato)tetraammineruthenium(III) Hexafluorophosphate[a]

Ru–O(2)	1.996 (3)	Ru–N(6)	2.118 (6)
Ru–N(2)	2.103 (4)	C(1)–C(2)	1.518 (8)
Ru–N(3)	2.102 (5)	C(1)–O(1)	1.216 (5)
Ru–N(4)	2.111 (6)	C(1)–O(2)	1.297 (5)
Ru–N(5)	2.104 (6)	C(2)–N(2)	1.490 (6)
O(2)–Ru–N(2)	81.8 (1)	N(3)–Ru–N(6)	91.1 (2)
O(2)–Ru–N(3)	89.7 (2)	N(4)–Ru–N(5)	89.0 (2)
O(2)–Ru–N(4)	90.1 (2)	N(4)–Ru–N(6)	91.6 (2)
O(2)–Ru–N(5)	87.8 (2)	N(5)–Ru–N(6)	91.6 (2)
O(2)–Ru–N(6)	178.1 (2)	O(2)–Ru–N(2)	81.8 (1)
N(2)–Ru–N(3)	89.7 (1)	C(2)–C(1)–O(1)	121.0 (4)
N(2)–Ru–N(4)	171.8 (2)	C(2)–C(1)–O(2)	116.4 (4)
N(2)–Ru–N(5)	91.9 (2)	O(1)–C(1)–O(2)	122.6 (4)
N(2)–Ru–N(6)	96.5 (2)	C(1)–C(2)–N(2)	111.1 (4)
N(3)–Ru–N(4)	89.0 (2)	Ru–O(2)–C(1)	117.5 (2)
N(3)–Ru–N(5)	176.7 (2)	Ru–N(2)–C(2)	108.1 (3)

[a] Esd's are in parentheses.

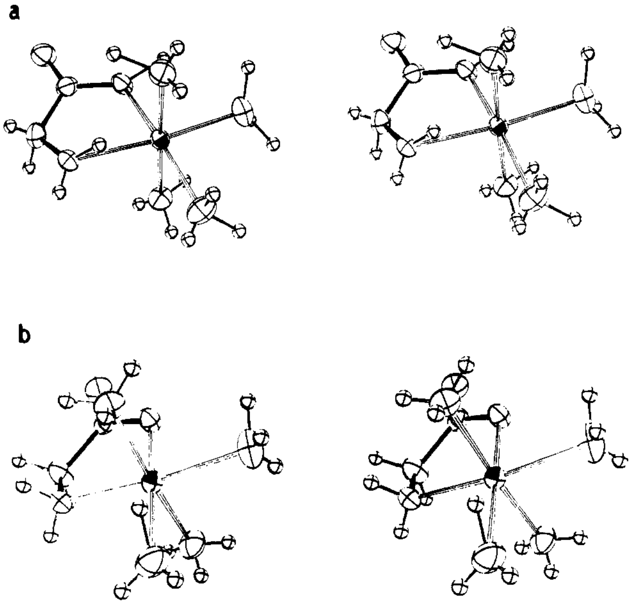

Figure 2. Stereoscopic drawings showing 50% probabilty ellipsoids of (a) (glycinamido)tetraammineruthenium(III) and (b) (glycinato)tetraammineruthenium(III).

imposed by the bidentate ligands. The angle X–Ru–N(2) is most affected by these constraints and is remarkably less than 90°. The other angles are much closer to the ideal octahedral geometry. The Ru–N(1) bond length (1.966 Å) in compound I is significantly shorter than other bond lengths between the metal and amino nitrogens. This shortening is ascribed to a stronger bond between the amido nitrogen and the metal ion (vide infra). The glycinamido and glycinato ligands are far from being planar. The torsion angles X–C1–C(2)–N(2) are 20.6° and 21.8° for I and II, respectively.

Discussion

It has been suggested recently[15] that deprotonated N-bound amido and urea complexes of transition-metal ions such as Ru(III), Co(III), Rh(III), and Cr(III) are stabilized by a resonance of the type

$$\underset{\mathrm{I}}{[\mathrm{M{-}NH{-}C(R){=}O}]^{2+}} \leftrightarrow \underset{\mathrm{II}}{[\mathrm{M{-}NH{=}C(R){-}O^{-}}]^{2+}}$$

Such a resonance implies a shortening of the C–N bond and a lengthening of the C–O bond. These expectations are not realized in the structure of the glycinamido chelate of ruthenium, where the C–O and the C–N bonds are very similar in length to typical analogous bonds in free amides[16] (Table VI).

Table VI presents also crystallographic results for C–N and C–O bonds of amido groups coordinated to Co(III) in two chelates:

---

(15) Fairlie, D. P.; Taube, H. *Inorg. Chem.* **1985**, *24*, 3199–3206.

(16) Robin, M. B.; Bovey, F. A.; Basch, H. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience: London, 1970; pp 1–72.

Table VI. Amide Group Bond Lengths in Ru(III) and Co(III) Amido and Peptido Chelates[a]

		chelate		
bond	free amides[b]	tetraammine(glycinamido)ruthenium(III)[c]	bis(glycylglycinato)cobalt(III)[d]	diammine(alanylglycylglycinato)cobalt(III)
C–O	1.24	1.244	1.26	1.266
C–N	1.34	1.334	1.30	1.315

[a] Bond lengths in Å. [b] Reference 16. [c] This work. [d] Reference 10.

Table VII. Carboxylato Group Bond Lengths in Ru(III) and Co(III) Glycinato and Peptido Chelates[a]

	chelate			
bond	tetraammine(glycinato)ruthenium(III)[b]	bis(glycylglycinato)cobalt(III)[c]	diammine(alanylglycylglycinato)cobalt(III)[d]	(triethylenetetramine)(glycinato)cobalt(III)[e]
C=O	1.216	1.23	1.248	1.233
C–O(–M)	1.297	1.29	1.297	1.284
Δ(C–O)[f]	0.081	0.06	0.049	0.051
M–O	1.996	1.93	1.96	1.914

[a] Bond lengths in Å. [b] This work. [c] Reference 9. [d] Reference 10. [e] Reference 11. An average of the five stereoisomers which are presented in these papers. [f] This represents the difference between the C–O bond lengths of the coordinated and uncoordinated oxygen atoms.

bis(glycylglycinato)cobalt(III)$^-$[9] and diammine(L-alanylglycylglycinato)cobalt(III).[10] These results show an increase in the C–O bond length and decrease in the C–N bond length, indicating a significant contribution of resonance form II.

The Ru–amido nitrogen bond in the tetraammineruthenium(III) chelate is shorter than the Ru–N bond of the amino group of glycinamide or of the ammonia ligands by ~0.16 Å (Table IV). In the bis(glycylglycinato)cobalt(III) chelate, the difference between the Co–NH_2 bond length and the Co–NH bond length amounts to 0.09 Å,[9] and in the diammine(alanylglycylglycinato)cobalt(III) chelate, the average difference between the Co–N of the ammonia and amine groups and the Co–NH of the amide group is ~0.10 Å.[10] The M–NH bond length is expected to be shorter than the M–NH_2R or M–NH_3 bonds because of the negative charge on the nitrogen, but in the Ru(III) complex the difference in bond lengths is much larger than in the Co(III) complexes. This indicates a stronger interaction between the amido nitrogen and Ru(III), which could result from a π interaction of the P lone pair on NH (the amido nitrogen is sp^2 hybridized, as also indicated by the C(2)–N(1)–Ru angle of 119.9°) and the half-filled t_{2g} orbital on Ru(III). This kind of interaction explains why resonance form II does not contribute significantly to the structure of the deprotonated amido group when it is coordinated to Ru(III) and is also responsible for the increased acidity of Ru(III) N-bound amido complexes as compared to the Co(III) analogues.[2,15] Such a π interaction cannot take place in the d^6 Co(III) complexes, where the t_{2g} orbitals of π symmetry are completely full.

A ligand to metal π charge transfer was implicated in the interaction between the $(NH_3)_5Ru^{III}$ and imidazole and guanine ligands and was suggested to explain the lower pK_a values of these ligands when bound to Ru(III) as compared to their pK_a values in analogous Co(III) complexes.[17] The same reasoning was applied in order to explain the short Ru–N bond in (1-methylcytosinato)pentaammineruthenium(III) as well as the lengthening of the cytosinato C–N bonds upon coordination to Ru(III).[18]

Margerum and his co-workers have discussed similar effects in amido complexes of Cu and Ni. They have determined the crystal structure of the Cu(III) complexes of tri-α-aminoisobutyric acid and compared it with the structures of Ni(II) and Cu(II) peptide complexes.[19] The Cu(III) M–L bonds are shorter than the equivalent bonds in the Ni(II) and Cu(II) complexes. In the Cu(II) and Ni(II) complexes, the C–O bonds lengthen while the C–N bond lengths decrease as compared to the case of free amides, due to a significant contribution of resonance form II. In the Cu(III) complex, the C–O and C–N bond lengths are unchanged from their values in free amides, because of the stronger Cu(III)–peptide nitrogen bonds, which favor resonance form I.

The stronger interaction between Cu(III) and the amido nitrogen can be attributed to the higher charge on Cu(III) and to a π interaction between the $2p_z$ orbital of nitrogen and the empty $4p_z$ orbital of the metal ion, which is not involved in σ bonds with ligands in a square-planar complex. This kind of interaction is less important in the d^9 Cu(II) complexes, which are not truly square planar and have one or two axial ligands.[20] The d^8 Ni(II) complexes are square planar, but the lower charge of the metal ion does not favor sharing of ligand π electrons.

The amido nitrogen–metal π interaction becomes stronger in the square-planar complexes of group 10, going down the periodic table, as the empty valence p_z orbitals become more extended This may explain the relative pK_a values of peptide nitrogens bound to the M(II) ions of this group: 8–9 for Ni(II), 2.5–3.5 for Pd(II), and 1–2 for Pt(II).[21]

Ligand to metal π bonding for amido nitrogens of deprotonated amine groups has been suggested for the conjugate base of Co(III)–amine complexes in the trigonal-bipyramid intermediate,[22] for square-planar Cu(III)–peptide complexes,[23] and for transition-metal–dialkylamides, $M{=}N(CH_3)_2$ (M = Ti, V, Mo)[24] and has been discussed in the molecular orbital treatment of $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt).[25]

An analogous effect is observed on comparing the influence of coordination of the carboxylate group to Ru(III) and to Co(III). The difference in the bond lengths of the two carboxylic C–O bonds is presented in Table VII for three Co(III) chelates, including a glycinato chelate,[11] and is compared with the results obtained in the present work for the Ru(III) glycinato complex. The two C–O bonds, which are equivalent in deprotonated free carboxylates, differ in the Ru(III) chelate by ~0.08 Å, whereas this difference in the Co(III) chelates amounts to only 0.05–0.06 Å. Thus, coordination to Ru(III) renders the two carboxylate oxygens more unequivalent than does coordination to Co(III). This indicates a stronger M–O interaction for M = Ru(III) than for M = Co(III), in spite of the fact that the Co(III) ion is smaller than the Ru(III) ion and makes a shorter contact with the oxygen bound to it than does Ru(III) (Table VII).

Acknowledgment. This research was supported by the Technion VPR Fund–New York Metropolitan R. Fund. We thank Johnson

---

(17) Brown, G. M.; Sutton, J. E.; Taube, H. *J. Am. Chem. Soc.* **1978**, *100*, 2767–2774.

(18) Clarke, M. J. *Inorg. Chem.* **1980**, *19*, 1103–1104.

(19) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021–1025.

(20) Falk, K. E.; Freeman, H. C.; Jansson, T.; Malmstrom, B. G.; Vangard, T. *J. Am. Chem. Soc.* **1967**, *89*, 6071–6077.

(21) Kirvan, G. E.; Margerum, D. W. *Inorg. Chem.* **1985**, *24*, 3017–3021 and references therein.

(22) Pearson, R. G.; Basolo, F. *J. Am. Chem. Soc.* **1956**, *78*, 4878–4883.

(23) Neubecker, T. S.; Kirksey, S. T.; Chellappa, K. L.; Margerum, D. W. *Inorg. Chem.* **1979**, *18*, 444–448.

(24) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273–280.

(25) Gray, H. B.; Ballhausen, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 260–265.

Matthey Chemicals Ltd. for the loan of $RuCl_3$.

Registry No. I, 85320-36-1; II, 85335-32-6.

Supplementary Material Available: Tables of anisotropic temperature factors (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
North-Eastern Hill University, Shillong 793003, India

Complex Peroxyuranates. Synthesis and Structural Assessment of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$

Manish Bhattacharjee, Mihir K. Chaudhuri,* and Ranendra N. Dutta Purkayastha

Received September 4, 1985

Yellow microcrystalline alkali-metal and ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and alkali-metal and ammonium dioxoperoxy(oxalato)uranate(VI) hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K), have been synthesized from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2\cdot 6H_2O$ with alkali-metal or ammonium hydroxide, AOH, with 30% H_2O_2 and aqueous sulfuric acid and oxalic acid solution, respectively, in the mole ratio $UO_2(NO_3)_2\cdot 6H_2O$:H_2O_2:SO_4^{2-} or $C_2O_4^{2-}$ of 1:111:5 or 1, at pH 6 maintained by the addition of the corresponding alkali-metal or ammonium hydroxide. Precipitation was completed by the addition of ethanol. IR and laser Raman spectra suggest that the O_2^{2-} and SO_4^{2-} ions in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ are bonded to the UO_2^{2+} center in a bridging and in a monodentate manner, respectively, while both the O_2^{2-} and $C_2O_4^{2-}$ ions in $[UO_2(O_2)C_2O_4]^{2-}$ bind the uranyl center in a bidentate chelated fashion. The complex peroxyuranates are diamagnetic and insoluble. The $A_2[UO_2(O_2)SO_4(H_2O)]$ compounds, unlike $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$, are stable up to 110 °C. Whereas H_2O in $A_2[UO_2(O_2)SO_4(H_2O)]$ is coordinated to the UO_2^{2+} center, it occurs as a water of crystallization in the corresponding peroxy oxalato compounds.

Introduction

Although uranium is the most important and useful of the actinide metals and is known to form simple peroxides,[1,2] its heteroligand peroxy chemistry seems to have been practically overlooked in earlier investigations.[1,2] This is probably because of the highly complicated nature of peroxyuranate chemistry[1] owing to the formation of a number of different species with a small variation of pH of the reaction solution. Peroxyuranates containing O_2^{2-}:U ratios of 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 were described in the literature,[1,2] of which $UO_2(O_2)\cdot nH_2O$ (n = 2, 4) appears to be the best characterized one. Recent experience in the field of peroxy–metal chemistry[3–6] advocates an enhanced stability of such compounds brought about by the coordination of heteroligands. Reports on heteroligand peroxyuranate compounds are rather scanty, except for the ones on (carbonato)- and (oxalato)peroxyuranates.[1]

The present work was undertaken to synthesize hitherto unknown peroxy(sulfato)uranates(VI) and improvise a direct route to peroxy(oxalato)uranates(VI), to make an assessment of their structures and to rationalize the IR and laser Raman spectra in terms of the modes of binding of O_2^{2-} and SO_4^{2-} or $C_2O_4^{2-}$ with the UO_2^{2+} center, and to make an internal comparison of the results to correlate with that of the previously reported $(NH_4)_2UO_4C_2O_4\cdot 3H_2O$.[7]

Experimental Section

The chemicals used were all reagent grade products. IR and laser Raman (LR) spectra were recorded on the instruments and by the methods described in our earlier papers.[3,6,8] LR spectra were recorded on solids owing to the insolubility of the compounds. Magnetic susceptibility measurements were made by the Gouy method; $Hg[Co(NCS)_4]$ was the calibrant. The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na). A 1.0-g (1.99-mmol) sample of $UO_2(NO_3)_2\cdot 6H_2O$ was dissolved in water (10–15 cm^3) followed by addition of 25% ammonium hydroxide solution or a concentrated solution of sodium hydroxide in the case of the Na^+ salt with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of alkali-metal ion or ammonium ion and nitrate. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of 2.5 M H_2SO_4 solution to obtain a clear solution, which was stirred for ca. 5 min. A 25-cm^3 (220.5-mmol) sample of 30% H_2O_2 was added, while the U:SO_4^{2-}:H_2O_2 ratio was maintained at 1:5:111, and the solution was stirred for ca. 15 min followed by careful addition of the corresponding alkali-metal or ammonium hydroxide solution, AOH (A = NH_4, Na), until the pH was raised to 6, whereupon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), in high yields. Each compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times), and finally dried in vacuo over concentrated H_2SO_4.

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K). The $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ compounds were prepared in a manner analogous to that described above for the synthesis of the peroxy(sulfato)uranate compounds. The two points of differences are that (i) a concentrated solution of oxalic acid ($H_2C_2O_4\cdot 2H_2O$) was used in lieu of the 2.5 M H_2SO_4 solution and (ii) a U:$C_2O_4^{2-}$:H_2O_2 ratio of 1:1:111 was maintained for the synthesis.

The amounts of reagents used for the syntheses and the yields of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A

---

(1) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 345.

(2) Ahrland, S.; Bagnall, K. W.; Brown, D.; Dell, R. M.; Eberle, S. H.; Keller, C.; Lee, J. A.; Liljenzin, J. O.; Mardon, P. G.; Marples, J. A. C.; Milner, G. W. C.; Philips, G.; Potter, P. E.; Rydberg, J. *The Chemistry of Actinides*; Pergamon: Elmsford, NY, 1975; Pergamon Texts in Inorganic Chemistry Vol. 10, p 249.

(3) Chaudhuri, M. K.; Ghosh, S. K. *Polyhedron* **1982**, *1*, 553; *Inorg. Chem.* **1982**, *21*, 4020; *Ibid.* **1984**, *23*, 534; *J. Chem. Soc., Dalton Trans.* **1984**, 507.

(4) Schwendt, P.; Joniakova, D. *Polyhedron* **1984**, *3*, 287.

(5) Djordjevic, C. *Chem. Br.* **1982**, *18*, 554. Djordjevic, C.; Craig, S. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 1283.

(6) Chaudhuri, M. K.; Das, B. *Polyhedron* **1985**, *4*, 1449. Bhattacharjee, M. N.; Chaudhuri, M. K.; Dutta Purkayastha, R. N. *J. Chem. Soc., Dalton Trans.* **1985**, 409.

(7) Krishna Prasad, N. S. *J. Inorg. Nucl. Chem.* **1961**, *21*, 379. Baskin, Y.; Krishna Prasad, N. S. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1385.

(8) Chaudhuri, M. K.; Ghosh, S. K.; Islam, N. S. *Inorg. Chem.* **1985**, *24*, 2706. Basumatary, J. K.; Chaudhuri, M. K.; Dutta Purkayastha, R. N.; Hiese, Z. *J. Chem. Soc., Dalton Trans.*, in press.

0020-1669/86/1325-2354$01.50/0