ligand is behaving as a Lewis acid, but is in the range found for NO^+ complexes (1.57–1.78 Å; see Table VI of ref 2). The Ir–N–O bond angle (163.5 (10)°), though far from 180°, is just within the range observed for NO^+ complexes (see Table VI of ref 2). Finally the large N–Ir–N′ bond angle can perhaps be accounted for by nonbonded interactions. The nonbonded contacts between the nitrosyl group and the *ortho*-hydrogen atoms of the triphenylphosphine groups are near those predicted from van der Waals radii.[27] We have calculated that these contacts would decrease considerably if the N–Ir–N′ bond angle were 109° 28′. The importance of these steric factors might be evaluated if the crystal structure of $Pt(CO)_2(P(C_6H_5)_3)_2$ were determined.

We have made many attempts to isolate crystals of the five-coordinate complex $IrI(NO)_2(P(C_6H_5)_3)_2$. However each time mixtures of $IrI(NO)_2(P(C_6H_5)_3)_2$ and $IrI_2(NO)(P(C_6H_5)_3)_2$ have been obtained. We wish to speculate that $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$ is able to react with lithium halides to give these unusual five-coordinate complexes for two reasons. First, the geometry of the cation is intermediate between tetrahedral and square planar and therefore the activation energy for formation of a five-coordinate complex is smaller than that for a relatively undistorted tetrahedral complex such as $Pt(CO)(P(C_6H_5)_3)_3$. Second, nitrosyl is an amphoteric ligand and the two electrons which exceed the inert-gas rule can be accommodated in antibonding nitrosyl orbitals rather than in metal–ligand σ-antibonding orbitals. The fact that nitrosyl is able to behave like an electron well in such reactions suggests some very interesting catalytic possibilities.

Acknowledgments.—We wish to thank Dr. K. W. Muir and Dr. N. C. Payne for their assistance and the National Science Foundation for financial support.

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[27] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, p 115.

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The Crystal and Molecular Structure of Hexakis(urea)titanium(III) Iodide

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The crystal structure of hexakis(urea)titanium(III) iodide, $Ti[OC(NH_2)_2]_6I_3$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined to a final unweighted *R* factor of 0.067 and a weighted *R* factor of 0.064 for 499 independent nonzero reflections. The salt crystallizes in the rhombohedral space group $R\bar{3}c$ with six formula units in a hexagonal unit cell of dimensions $a = 17.67\ (2)$ Å and $c = 14.15\ (2)$ Å. The structure consists of octahedral complex ions having rigorous D_3 point symmetry and essentially linear arrays of iodide ions parallel to the crystallographic threefold axis. The titanium–oxygen bond distance is 2.014 (5) Å. There are significant distortions of the coordination polyhedron from the idealized O_h symmetry and from the D_{3d} model often assumed for trigonally distorted octahedral complexes. The three independent O–Ti–O angles are 90.5 (2), 86.4 (3), and 92.8 (3)°, and the angles between successive pairs of Ti–O bonds viewed in projection along the threefold axis are 54.4 and 65.6°. The stability of this complex to aerial oxidation apparently arises from intramolecular hydrogen bonding involving the urea molecules and also hydrogen bonds involving the iodide ions. The d-orbital energy level sequence for a crystal (ligand) field of D_3 symmetry, where the inclination of metal–ligand bond to the threefold axis is 54.74°, can be described entirely in terms of the parameter *Dq*, and the ground state for a d^1 complex ion is $^2A_1$.

Introduction

Coordination compounds of titanium(III) have long occupied a prominent place in the development at various levels of sophistication of crystal and ligand field theory. Despite this fact, however, there is a paucity of accurate structural information from X-ray measurements on their detailed stereochemistry in the solid, principally because the majority of such compounds are highly unstable with respect to oxidation and many hydrolyze rapidly in the presence of moisture. The isolation and handling of suitable single crystals is thus a difficult operation.

One of the more stable species is the hexakis-urea complex ion which was first isolated as the perchlorate salt[2] and subsequently as the iodide.[3] One of the interesting features of the latter compound is its marked stability relative to other titanium(III) species, and a preliminary report of the crystal structure, in the form of a two-dimensional projection, has already been given.[4] This preliminary work did not reveal the origin of the stability of the complex, however, and we have therefore carried out a more detailed study, both to investigate this point and to assess the nature of the distortion from regular octahedral symmetry, which is indicated by the observed variation

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[1] Fulbright Scholar at University of Southampton, 1968–1969.

[2] G. A. Barbieri, *Atti Reale Accad. Lincei.*, **24**, 916 (1915).

[3] H. Hartmann, H. L. Schlafer, and K. H. Hansen, *Z. Anorg. Allgem. Chem.*, **284**, 153 (1956).

[4] A. Linek, J. Siskova, and L. Jensovsky, *Collection Czech. Chem. Commun.*, **31**, 4453 (1966).

of magnetic moment with temperature.[5] Two ligand field models of lower than O_h symmetry, namely, those of D_{4h} and D_{3d} symmetries, respectively, are commonly used to explain similar departures of the magnetic properties of octahedral complexes from those predicted for the T ground-state terms of the undistorted geometry.[6,7] As a result of this investigation we find that an alternative distortion, namely, that toward a trigonal prism, symmetry D_3, can be of equal validity.

Experimental Procedures

Crystalline $Ti[OC(NH_2)_2]_6I_3$ was prepared as described by Hartmann and coworkers.[3] *Anal.* Calcd for $TiO_6C_6N_{12}H_{24}I_3$: I, 48.25; Ti, 6.07; C, 9.13; N, 21.31; H, 3.07. Found: I, 48.31; Ti, 6.02; C, 9.11; N, 21.24; H, 3.28. The well-formed deep blue crystals have an acicular habit. Two types of crystal were found; some are very nearly regular hexagons in cross section, while others have alternate faces more prominently developed. When developed, the end faces are inclined at *ca.* 120° to the needle axis.

On the basis of precession photographs of crystals mounted around the needle axes and taken using Mo Kα radiation, it appeared that crystals of the first type were twinned, the two lattices having a common c^* axis, with one lattice in the obverse and one in the reverse orientation. These crystals were not examined further. Precession photographs of a crystal of the second type, however, could be indexed unambiguously on the basis of a rhombohedral or hexagonal lattice, the latter being used here. The systematic absences found from levels $h0l$, $h1l$, and hhl and from an $hk0$ Weissenberg photograph were: for hkl, $-h + k + l \pm 3n$; and for $h0l$, $l \pm 2n$. The Laue symmetry is $\bar{3}$m. These observations are consistent with space groups R$\bar{3}$c and R3c, the former being that reported by Linek, Siskova, and Jensovsky.[4] Preliminary cell dimensions agreed with those given by these workers and their experimental value for the density of 2.06 g cm^{-3} (determined pycnometrically) was assumed for this analysis.

A needle-shaped crystal of the second type and having overall dimensions 0.14 × 0.35 mm was selected for intensity measurement and was mounted with the c^* (needle) axis coincident with the ϕ axis of a General Electric quarter-circle XRD-6 manually operated diffractometer. The source to crystal and crystal to detector distances were 14.6 and 16.5 cm, respectively. The unit cell dimensions obtained from the 2θ values of the $h00$ and $00l$ reflections measured at a takeoff angle of 1°, using Zr-filtered Mo Kα radiation (λ 0.7107 Å), at 16° are a = 17.67 (2) Å and c = 14.15 (2) Å. With six formula units per hexagonal unit cell, the calculated density is 2.03 ± 0.01 g cm^{-3}, in good agreement with that quoted above. In the absence of disorder, the cation is required to have point symmetry 32 (D_3) or $\bar{3}$ (D_{3d}) by space group R$\bar{3}$c and threefold symmetry (C_3) by R3c.

The integrated intensities of 529 independent reflections within the sphere $2\theta_{Mo} \leqslant 45°$ were measured at an X-ray takeoff angle of 1° using the θ–2θ scan technique and a scan rate of 2°/min. A scintillation counter equipped with pulse height analyzer, set for a 95% window centered on the Mo Kα peak, was used as detector. The instrument settings were computed using GESET[8] which also calculates the scan range according to $\Delta(2\theta) = A + B \tan \theta$[9] where A and B had the values 1.80 and 1.0°, respectively. Stationary background counts B_1 and B_2 were taken at each limit of the scan for $(2\theta)/4$ min and the net intensity was evaluated as $I = P - (B_1 + B_2)$ where P is the total integrated count. The data collection was monitored by checking the intensity of a standard reflection after each group of approximately ten reflections and no significant change within a level of *ca.* 3% was observed. In addition to the independent set of data $hkil$, the intensities of *ca.* 200 reflections in the neighboring sector of reciprocal space and of the form $\bar{h}\bar{i}\bar{k}l$ were also measured, and no significant differences between related pairs were observed. While the reflections $hkil$ comprise the complete data set for both space groups R$\bar{3}$c and R3c in the absence of anomalous scattering, when the latter effect is important, the complete data set for the polar space group includes the $hki\bar{l}$ reflections, the point symmetry being 3m. With our present experimental arrangement, these reflections occur at negative 2θ angles and no measurements were made in this region.

The dimensions of the crystal faces, which had indices of the form (100), (010), (110), and (001), were carefully measured and absorption corrections were applied (μ = 40.8 cm^{-1}).[10] However, these corrections were small, the transmission factors varying only from 0.805 to 0.823. The results of ϕ scans of the $00l$ reflections had previously indicated that absorption errors arising from the noncylindrical symmetry of the crystal were very small. The intensity data were assigned standard deviations according to the formula $\sigma(I) = [P + B_1 + B_2 + (pI)^2]^{1/2}$, with p given the value 0.04.[11] Thirty reflections had net intensities equal to or less than their calculated standard deviations. The intensities were reduced to F^2 values by application of Lorentz and polarization factors.

Solution and Refinement

A three-dimensional Patterson map gave a set of highest peaks which were consistent with the assignment of the iodide ions to the 18(e) special positions in space group R$\bar{3}$c,[12] with x = 0.375. Location of the Ti–I vectors then indicated that the metal atoms would be situated in the 6(a) special positions of this space group, symmetry 32 (D_3), rather than the 6(b) positions. Both of these observations are in agreement with the preliminary work of Linek, *et al.*,[4]

While such a vector set can also be interpreted in terms of the noncentrosymmetric space group, the set of heavy atoms so derived would have the symmetry of the centric group (either very closely or exactly) even though the structure as a whole might not possess a center of symmetry. Consequently the criterion for recognizing the polar space group mentioned earlier, *viz.*, the nonequivalence of the $hkil$ and $hki\bar{l}$ reflections, would not be fulfilled considering only the heavy atoms as anomalous scatterers. An electron density map phased on the heavy atoms clearly indicated the urea molecules and suggested that the correct space group is R$\bar{3}$c. This was confirmed on refinement.

Two cycles of full-matrix least-squares refinement, with unit weighting, of the positional and isotropic thermal parameters of the six atoms plus a scale factor (20 variables) led to a conventional residual, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.12 and a weighted residual, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, of 0.122. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the atomic

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[5] D. J. Machin, K. S. Murray, and R. A. Walton, *J. Chem. Soc., A*, 195 (1968).

[6] B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).

[7] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1965).

[8] GESET, a diffractometer setting program by J. Kraut and S. T. Freer, included in the X-Ray 63 program system, as adapted for use on the Atlas computer, Harwell, England. This system also incorporates the Busing–Martin–Levy full-matrix least-squares program ORFLS, which was used for all refinements, and the error function program ORFFE, which was used for calculating the orientations and magnitudes of the thermal ellipsoids.

[9] L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962).

[10] Computed using ABSCOR—an absorption correction program by N. W. Alcock, based on a method by J. De Meulenaer and H. Tompa, *ibid.*, **19**, 1014 (1965).

[11] P. W. R. Corfield, R. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[12] "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Ti(OC(NH_2)_2)_6I_3$[a]

Atom	x	y	z	B_{11} or B[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	0.0	0.0	0.250	4.63 (18)	4.63[c]	3.82 (17)	2.32	0.0	0.0
O	0.1078 (3)	0.0584 (3)	0.1685 (4)	3.48 (22)	2.90 (24)	5.04 (27)	1.53 (18)	0.68 (19)	−0.16 (19)
C	0.1633 (5)	0.0407 (5)	0.1331 (5)	3.34 (36)	3.35 (35)	3.73 (36)	1.83 (31)	0.93 (28)	−0.05 (28)
N(1)	0.2398 (4)	0.1029 (5)	0.1101 (7)	3.55 (33)	3.61 (31)	8.16 (50)	1.88 (27)	1.53 (30)	0.52 (33)
N(2)	0.1442 (5)	−0.0417 (4)	0.1166 (7)	3.99 (31)	3.93 (35)	10.43 (60)	1.36 (30)	−3.66 (37)	−1.47 (35)
I^-	0.37023 (4)	0.0	0.250	6.26 (8)	3.66 (6)	5.64 (7)	1.83	−0.37 (1)	−0.75
H(11)	0.287	0.089	0.088	4.0					
H(12)	0.240	0.158	0.119	4.0					
H(21)	0.183	−0.057	0.105	4.5					
H(22)	0.089	−0.081	0.148	4.5					

[a] Estimated standard deviations in last significant digits given in parentheses; none is given for parameters fixed by symmetry or for hydrogen atoms. The latter were not refined. [b] The form of the anisotropic thermal ellipsoid is given by $\exp[-(\Sigma_{ij}h_ih_jr_ir_jB_{ij})/4]$ where r_i is the ith reciprocal axis and $i, j = 1$–3. [c] The point symmetries of the special positions 18(e) and 6(a) require that for the iodide ion, $B_{22} = 2B_{12}$ and $B_{23} = 2B_{13}$ and for the titanium atom, $B_{11} = B_{22} = 2B_{12}$ and $B_{13} = B_{23} = 0$.

scattering factors used for all nonhydrogen atoms were those tabulated by Cromer and Waber.[13] Anomalous dispersion corrections for titanium and iodine[14] were applied to the calculated structure factors. Two cycles of refinement with anisotropic thermal parameters were then carried out (a total of 44 variables) and these led to values of R_1 and R_2 of 0.076 and 0.09 with unit weights. The drop in R_2 represents a significant improvement on adopting the aniostropic model at the 99.5% confidence level.[15]

At this point, a difference Fourier map was computed in an attempt to locate the four crystallographically independent hydrogen atoms. There were only six peaks greater than 0.5 $e^-/Å^3$ and two of these could be assigned to hydrogen atoms associated with one nitrogen atom. Plausible positions for the other two hydrogens were located in regions of density greater than 0.4 $e^-/Å^3$; in agreement with studies of the free urea molecule, the four atoms were found to be nearly coplanar with the "heavy" atoms. These atoms were accordingly added to the model and assigned isotropic thermal parameters equal to the average values of the thermal ellipsoids of their respective nitrogen atoms. A structure factor calculation gave a value of R_1 of 0.074, the hydrogen scattering factor used being that tabulated by Stewart, Davidson, and Simpson.[16]

Further refinement was carried out including weights for the individual reflections calculated from the standard deviations of the intensities according to $w^{1/2} = 2(Lp)F_o/\sigma(I)$, where L and p are the Lorentz and polarization factors. Nine reflections showing pronounced errors attributable to primary extinction were removed and four cycles of anisotropic refinement lowered the values of R_1 and R_2 to 0.067 and 0.064 for the observed data, at which point convergence was reached. All reflections, apart from those mentioned above, were included in the least-squares refinement and the final residual, R_1, for all reflections was 0.097. No parameter changed by more than 0.18 of its estimated standard deviation during the final cycle. A final difference Fourier map showed no region exceeding ±0.3 $e^-/Å^3$ and regions approaching these limits were associated with the iodide ions and titanium atoms. The standard deviation of an observation of unit weight had the rather high value of 3.15, suggesting that the standard deviations of the intensities had been underestimated. However, the contributions to $\Sigma w(|F_o| - |F_c|)^2$ were reasonably constant for all classes of reflection distributed among $|F_o|$ and $(\sin \theta)/\lambda$, so that the weighting scheme appears to show no bias to this extent.

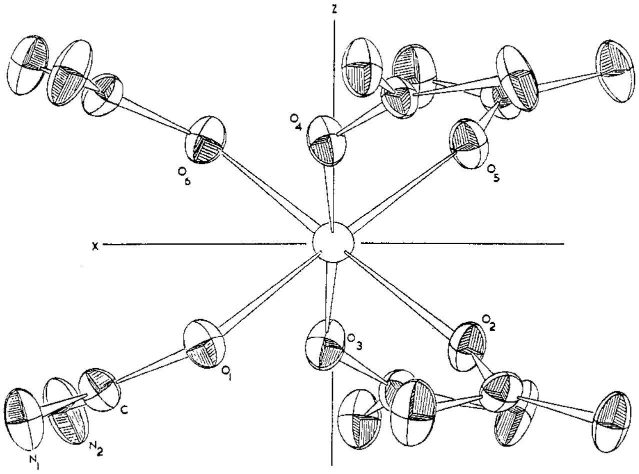

Figure 1.—A perspective view of the $Ti(OC(NH_2)_2)_6^{3+}$ ion showing the relative magnitudes and orientations of the thermal ellipsoids.

The final positional and anisotropic thermal parameters are listed in Table I, along with the standard deviations derived from the inverse matrix. Table II lists the final values of F_o and F_c in electrons.

Results and Discussion of Structure

A perspective drawing of the octahedral complex cation projected onto (010) is shown in Figure 1. The root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids are listed in Table III and the orientations of these ellipsoids are illustrated in Figure 1. The pattern of thermal motion seems physically reasonable.

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(13) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(14) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(15) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Ti(OC(NH_2)_2)_6I_3$ (IN ELECTRONS)

k	l	F_o	F_c
* h = 0 *			
0	12	223	232
1	14	20	18
2	10	167	175
3	12	201	215
4	14	9	11
5	10	191	193
6	12	95	89
8	10	182	187
9	12	55	52
11	10	208	212
* h = 1 *			
0	4	368	405
1	0	52	57
1	6	287	311
1	9	287	303
1	12	41	45
1	15	80	82
2	2	266	281
2	5	245	250
2	8	14	4
2	11	80	83
2	14	19	22
3	4	36	33
3	7	242	248
3	10	56	53
3	13	54	53
4	3	310	350
4	6	56	52
4	9	192	196
4	12	38	38
5	2	126	132
5	5	132	139
5	8	15	15
5	11	45	48
5	14	20	15
6	1	322	363
6	4	75	73
6	7	231	238
6	10	106	112
6	13	102	100
7	3	130	126
7	6	36	22
7	9	27	27
7	12	32	33
8	2	15	6
8	5	17	5
8	8	16	8
8	11	18	7
9	1	333	352
9	4	81	80
9	7	239	243
9	10	66	64
10	3	91	92
10	6	16	6
10	9	28	27
11	2	37	38
11	5	78	82
11	8	18	3
12	1	193	201
12	4	103	109
12	7	121	118
13	3	33	33
13	6	60	58
14	2	91	98
14	5	108	118
15	1	48	41
15	4	37	23
* h = 2 *			
0	2	305	318
0	8	124	123
0	14	62	64
1	1	135	126
1	4	214	220
1	7	101	94
1	10	65	64
1	13	66	62
2	0	268	301
2	6	116	115
2	9	195	204
2	12	35	25
3	5	19	10
3	8	217	219
3	11	8	7
3	14	73	74
4	4	63	65
4	7	263	265
4	10	66	65
4	13	96	99
5	3	187	190
5	6	14	21
5	9	138	144
5	12	18	18
6	2	370	411
6	5	78	77
6	8	167	158
6	11	31	28
7	1	409	475
7	4	113	114
7	7	291	305
7	10	81	83
7	13	92	88
8	3	60	59
8	6	137	133
8	9	47	43
8	12	53	51
9	2	64	61
9	5	76	75
9	8	49	45
9	11	45	46
10	1	280	289
10	4	113	113
10	7	163	163
10	10	19	1
11	3	16	9
11	6	123	119
11	9	19	7
12	2	61	66
12	5	117	128
12	8	31	30
13	1	117	124
13	4	18	3
13	7	129	125
14	0	97	98
14	3	29	43
14	6	82	84
15	2	25	30
* h = 3 *			
0	6	466	543
0	12	218	225
1	2	237	241
1	5	198	197
1	8	84	75
1	11	77	81
1	14	19	7
2	1	200	205
2	4	283	294
2	7	134	127
2	10	142	144
3	3	48	29
3	6	380	412
3	9	47	43
3	12	116	111
4	2	66	76
4	5	232	255
4	8	29	29
4	11	90	94
4	14	9	12
5	1	27	28
5	4	424	493
5	7	18	4
5	10	213	214
5	13	19	16
6	3	182	185
6	6	84	79
6	9	67	69
6	12	43	38
7	2	38	37
7	5	110	111
7	8	16	17
7	11	73	74
8	1	24	14
8	4	338	358
8	7	16	18
8	10	179	176
9	0	24	27
9	3	111	108
9	6	18	15
9	9	76	81
10	2	128	132
10	5	76	72
10	8	123	136
11	1	17	13
11	4	155	151
11	7	18	17
12	3	113	110
12	6	17	11
13	2	153	162
13	5	20	2
14	1	64	63
14	4	90	94
* h = 4 *			
0	4	122	116
1	0	227	246
1	3	317	347
1	6	86	80
1	9	178	189
1	12	55	51
2	2	235	227
2	5	312	323
2	8	27	21
2	11	133	139
2	14	32	22
3	1	234	251
3	4	159	168
3	7	177	182
3	10	73	63
3	13	54	55
4	0	179	183
4	3	82	81
4	6	100	104
4	9	32	28
4	12	36	33
5	2	17	8
5	5	195	219
5	8	70	73
5	11	77	83
6	1	365	389
6	4	124	121
6	7	201	197
6	10	61	62
7	0	17	17
7	3	102	104
7	6	78	78
7	9	17	13
7	12	22	13
8	2	86	82
8	5	84	76
8	8	57	52
8	11	19	26
9	1	173	173
9	4	139	145
9	7	142	148
9	10	27	28
10	3	186	181
10	6	47	47
10	9	79	80
11	2	60	59
11	5	53	56
11	8	24	22
12	1	107	107
12	4	24	26
12	7	53	45
13	3	100	107
* h = 5 *			
0	8	407	421
0	14	78	85
1	1	245	267
1	4	34	18
1	7	165	161
1	10	88	88
1	13	61	61
2	0	14	2
2	3	179	187
2	6	89	82
2	9	125	125
2	12	18	6
3	2	320	378
3	5	43	40
3	8	257	276
3	11	18	24
4	1	274	297
4	4	34	25
4	7	157	154
4	10	17	6
4	13	65	59
5	0	268	270
5	3	144	147
5	6	126	117
5	9	45	47
5	12	78	82
6	2	289	315
6	5	98	98
6	8	151	148
6	11	36	33
7	1	173	176
7	4	96	99
7	7	130	125
7	10	27	25
8	0	312	336
8	3	57	55
8	6	171	168
8	9	19	7
9	2	106	115
9	5	61	63
9	8	78	76
10	1	147	152
10	4	18	16
10	7	92	92
11	0	173	200
11	3	24	28
11	6	169	171
12	2	31	24
12	5	96	104
13	1	34	40
* h = 6 *			
0	0	283	323
0	6	262	262
0	12	67	68
1	2	298	332
1	5	344	371
1	8	16	15
1	11	141	139
2	1	26	22
2	4	233	227
2	7	37	35
2	10	136	137
2	13	19	24
3	0	136	145
3	3	140	132
3	6	123	118
3	9	43	44
3	12	60	64
4	2	95	93
4	5	299	301
4	8	90	84
4	11	100	106
5	1	24	17
5	4	222	224
5	7	24	18
5	10	125	124
6	0	169	170
6	3	64	70
6	6	61	49
6	9	123	126
7	2	52	47
7	5	113	115
7	8	18	19
7	11	54	52
8	1	19	11
8	4	171	179
8	7	25	24
8	10	102	93
9	0	66	57
9	3	197	197
9	6	51	49
9	9	100	102
10	2	85	88
10	5	34	32
11	1	72	72
11	4	128	128
12	3	116	108
* h = 7 *			
0	4	171	159
1	0	51	47
1	3	131	124
1	6	33	23
1	9	27	25
1	12	19	9
2	2	210	233
2	5	280	297
2	8	93	92
2	11	144	146
3	1	115	115
3	4	14	2
3	7	101	101
3	10	23	16
4	3	152	145
4	6	122	122
4	9	84	88
4	12	20	2
5	2	33	35
5	5	158	165
5	8	86	96
5	11	73	70
6	1	165	163
6	4	20	10
6	7	91	92
6	10	19	12
7	0	132	106
7	3	193	195
7	6	113	118
7	9	108	109
8	2	17	12
8	5	23	23
8	8	50	47
9	1	40	42
9	4	18	2
9	7	19	14
10	3	135	134
10	6	40	40
11	2	23	20
* h = 8 *			
0	2	445	517
0	8	375	385
1	1	53	55
1	4	21	13
1	7	54	48
1	10	36	33
2	0	140	138
2	3	33	25
2	6	104	97
2	9	28	31
2	12	51	50
3	2	415	469
3	5	10	18
3	8	230	241
3	11	19	1
4	1	77	60
4	4	84	74
4	7	73	71
4	10	7	8
5	3	16	3
5	6	171	161
5	9	19	10
6	2	208	223
6	5	17	3
6	8	98	98
7	1	78	78
7	4	17	1
7	7	37	36
8	0	263	270
8	3	46	19
8	6	197	192
9	2	48	51
9	5	19	2
10	1	38	41
10	4	65	62
* h = 9 *			
0	0	27	15
0	6	69	62
0	12	8	4
1	2	121	131
1	5	276	291
1	8	60	72
1	11	118	123
2	1	52	49
2	4	112	104
2	7	47	46
2	10	43	40
3	3	178	181
3	6	55	49
3	9	67	67
4	2	57	60
4	5	139	156
4	8	42	37
5	1	59	49
5	4	51	51
5	7	69	67
5	10	51	48
6	3	207	207
6	6	84	77
6	9	87	93
7	2	18	13
7	5	92	96
7	8	9	5
8	1	55	45
8	4	24	23
9	0	80	61
9	3	146	152
* h = 10 *			
0	4	183	161
1	0	44	39
1	3	89	81
1	6	87	80
1	9	59	62
2	2	91	92
2	5	214	224
2	8	52	54
2	11	85	85
3	1	103	99
3	4	86	85
3	7	18	6
3	10	48	43
4	0	19	10
4	3	126	117
4	6	36	28
4	9	73	70
5	2	19	17
5	5	139	139
5	8	19	8
6	1	27	20
6	4	64	51
6	7	19	12
7	0	82	81
7	3	150	157
7	6	47	42
8	2	28	27
* h = 11 *			
0	2	324	341
0	5	201	198
1	1	102	100
1	4	38	42
1	7	53	52
1	10	51	47
2	0	182	189
2	3	53	50
2	6	173	169
2	9	19	21
3	2	215	234
3	5	18	11
3	8	151	155
4	1	120	126
4	4	59	56
4	7	69	63
5	3	27	21
5	6	164	167
6	2	57	63
6	5	34	39
7	1	37	29
7	4	9	8
* h = 12 *			
0	0	90	92
0	6	24	17
1	2	64	71
1	5	167	176
1	8	60	66
2	1	161	158
2	4	18	4
2	7	99	91
3	0	59	46
3	3	90	80
3	6	49	43
4	2	73	72
4	5	37	34
5	1	64	61
5	4	17	16
6	0	71	81
6	3	109	107
* h = 13 *			
0	4	251	253
1	0	17	3
1	3	81	81
1	6	47	37
2	2	18	26
2	5	78	82
3	1	23	5
3	4	159	156
4	0	62	55
4	3	141	144
5	2	20	14
* h = 14 *			
0	2	223	229
0	8	81	68
1	1	107	117
1	4	8	4
1	7	83	81
2	3	35	36
2	6	84	77
3	2	65	70
4	1	93	96
* h = 15 *			
0	0	43	41
0	6	53	48
1	2	21	3
2	1	140	135

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å) ALONG THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS

Atom	Major axis	Intermed axis	Minor axis
Ti	0.242 (6)	0.242	0.220 (5)
O	0.263 (7)	0.202 (7)	0.189 (7)
C	0.241 (10)	0.207 (11)	0.169 (10)
N(1)	0.331 (10)	0.212 (9)	0.195 (10)
N(2)	0.392 (11)	0.246 (10)	0.168 (11)
I^-	0.300 (3)	0.273 (1)	0.208 (1)

TABLE IV

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) IN $Ti(OC(NH_2)_2)_6I_3$[a]

(a) Coordination Polyhedron

Ti–O	2.014 (5)	O(1)–Ti–O(5)	175.2 (3)
O(1)–Ti–O(2)	90.5 (2)	O(1)–Ti–O(4)	54.4 (2)[b]
O(1)–Ti–O(4)	86.4 (3)	O(1)–Ti–O(6)	65.6 (2)[b]
O(1)–Ti–O(6)	92.8 (3)	O–Ti–axis	55.1 (2)

(b) Urea Molecule

O–C	1.273 (9)		
C–N(1)	1.286 (10)	C–N(2)	1.331 (10)
N(1)–H(11)	1.03	N(2)–H(21)	0.90
N(1)–H(12)	0.98	N(2)–H(22)	0.96
O–C–N(1)	119.9 (7)		
O–C–N(2)	120.6 (7)	N(1)–C–N(2)	119.4 (8)
C–N(1)–H(11)	120	C–N(2)–H(21)	122
C–N(1)–H(12)	107	C–N(2)–H(22)	110
H(11)–N(1)–H(12)	132	H(21)–N(2)–H(22)	121

Equation of Weighted Least-Squares Plane through O, C, N(1), and N(2):[c] $0.328X - 0.240Y + 0.914Z = 2.702$ Å

Distances of Atoms from Plane (Å × 10^3): O, −2; C, 12; N(1), −4; N(2), −4; H(11), 97; H(12), −123; H(21), 200; H(22), 191

[a] Standard deviations in least significant figures given in parentheses. [b] Angles projected onto the (001) plane—see text. [c] In terms of cartesian coordinates where Y and Z are coincident with the b and c crystallographic axes. Weights calculated according to $w_i = 1/(a\sigma_{x_i} b\sigma_{y_i} c\sigma_{z_i})^{2/3}$ for the ith atom.

Interatomic distances and bond angles and their standard deviations are given in Table IV. Examination of the O–Ti–O bond angles listed here indicates that there are significant distortions of the TiO_6 coordination polyhedron from O_h and from D_{3d} symmetry. The symmetry of the polyhedron and of the whole complex ion is required to be D_3 from space group requirements and this is the maximum observed point symmetry. The deviation can be seen in Figure 1, in the departure from 180° of the bond angle O(4)–Ti–O(3) and less noticeably of the two related angles. When viewed in projection along the threefold axis, as in Figure 2, the three oxygen atoms above the plane of the titanium are rotated with respect to the three oxygen atoms below the plane, from the angle of 60° required for O_h or D_{3d} point symmetry, by approximately 5.6°. Carried to its limit, such a rotation would produce a trigonal prism.

By contrast, there is no significant deviation from 90° of the bond angles at titanium within one threefold set, the angle of inclination of the Ti–O bonds to the threefold axis being 55.1 (2)°, compared to the idealized angle of 54.74°. The type of distortion commonly assumed for the interpretation of magnetic data of "trigonal" octahedral complexes, *i.e.*, compression or elongation along the threefold axis,[6,7] is thus virtually absent.[17]

The Ti–O bond distance is 2.014 (5) Å and is shorter than might be anticipated. The Ti–O distance in $(TiBr_3)_2 \cdot 3C_4H_{10}O_2$ is 2.10 (8) Å, but the accuracy of this determination is not very great.[18] The titanium atom lies 0.53 Å out of the plane of the urea molecule, but such a deviation would not exclude the metal from being extensively involved in a delocalized system of π bonding with the ligand. Evidence for such an interaction is obtained from the magnetic data.[19] The Ti–O–C angle is 138.4 (5)°.

The geometry of the urea molecule differs from that of free urea in that the two C–N distances

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[17] This is, of course, true only for the atoms comprising the first coordination sphere. However, the ligand field effects arising from more distant atoms are very small and seldom considered.

[18] G. W. A. Fowles, T. E. Lester, and J. S. Wood, *J. Inorg. Nucl. Chem.*, **31**, 657 (1969).

[19] P. H. Davis and J. S. Wood, *Chem. Phys. Letters*, **4**, 466 (1969).

are significantly different, the difference being 0.045 (10) Å. The bond *trans* to the metal is the shorter and this can presumably be attributed to the redistribution of electron density on coordination of the ligand to the metal atom, the two C–N bonds no longer being equivalent in any bonding scheme. The C–O and C–N distances in crystalline urea have been given as 1.268 (7) and 1.326 (6) Å[20] from an X-ray study and as 1.243 (6) and 1.351 (7) Å[21] from a neutron diffraction study. The carbonyl bond distance might be expected to be longer in coordinated urea than in the free molecule, but compared with the X-ray data for the latter, there is no significant change.[20]

Intermolecular Packing and Hydrogen Bonding.—As noted earlier, one of the purposes of the analysis was to examine the role of hydrogen bonding in stabilizing the complex cation. Figures 2 and 3 show portions of the structure projected onto (001) and indicate an extensive system of hydrogen bonds. The structure consists of chains of $Ti(OC(NH_2)_2)_6^{3+}$ units stacked along the crystallographic *c* axis, each chain being separated from its neighbors and surrounded by six almost linear chains of iodide ions. The $I^- \cdots I^-$ distance along the chains is 4.85 Å.

Three of the four independent hydrogen atoms are involved in hydrogen bonding, the two attached to nitrogen N(1) being bonded to the iodide ions, while the six hydrogens of type H(22) (one independent) are bonded to the oxygen atoms of neighboring urea molecules in the same threefold set, *i.e.*, N(2)–H(22)$\cdots$O(3). The nitrogen–oxygen distance is 3.068 (10) Å compared with 3.034 (5) Å for a similar N–H$\cdots$O interaction in free urea[21] and is in the middle of the range of reported values.[22] The distance H(22)$\cdots$O(3) is 2.27 Å. The hydrogen bonds N$\cdots$I form a complete three-dimensional network and are presumably responsible for the stability of this complex compared to the perchlorate salt. Each iodide ion is involved in four such bonds, two (*e.g.*, $N_1 \cdots I_B$) of length 3.675 (5) Å and two (*e.g.*, $N_1 \cdots I_A$) of length 3.695 (5) Å. The relevant hydrogen–iodine distances are 2.84 and 2.79 Å and are 0.3–0.4 Å less than the sum of the van der Waals radii.[23] These bonds therefore appear to be quite strong. Figure 3 illustrates the manner in which each iodide ion is hydrogen bonded to four different $Ti(OC(NH_2)_2)_6^{3+}$ ions; *e.g.*, I^- with $z = {}^5/_{12}$ "connects" cations having metal atom *z* fractional coordinates of $^1/_{12}$, $^1/_4$, $^7/_{12}$, and $^3/_4$. All other intramolecular and intermolecular distances and specifically those involving H(21) appear to be normal for nonbonded interactions.

Crystal Field Energy Levels.—The d-orbital energy level sequence for trigonally distorted octahedral molecules is well known and can be described in terms of three crystal field parameters, *Dq*, *Dσ*, and *Dτ*.[24] The type of distortion described above does not seem to have been discussed previously, however, apart from the observation of Figgis, who noted that such a "twisting" of the octahedron does not introduce spherical harmonics of the type Y_2^0 into the expression for the crystal field potential.[25] This is in fact the case, and the calculation in this instance can be parametrized using solely *Dq*. As for the D_{3d} trigonally distorted octahedron, there are two doubly degenerate (e) orbitals and a nondegenerate (a) orbital, but in the

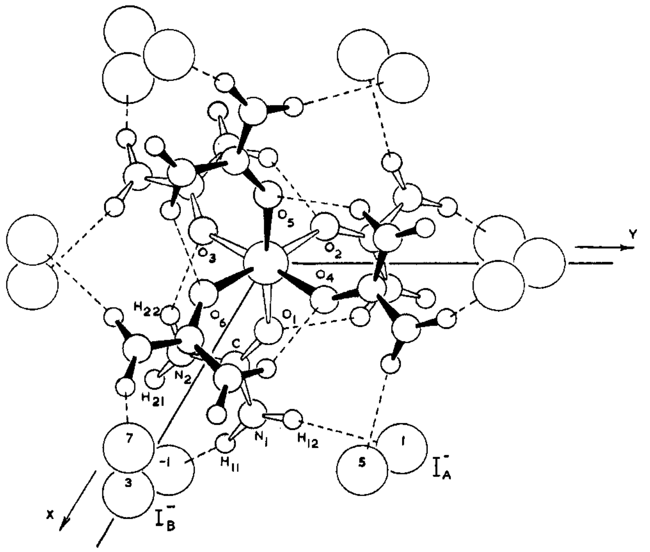

Figure 2.—One $Ti(OC(NH_2)_2)_6^{3+}$ ion and its immediate environment projected onto (001). The metal atom is situated at 0, 0, $^1/_4$ and all the hydrogen bonds to neighboring iodide ions (denoted by their *z* fractional coordinates in 12ths) are illustrated.

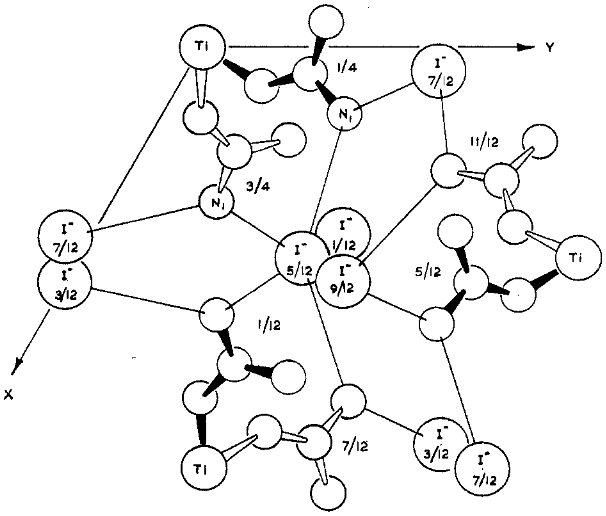

Figure 3.—A portion of the structure projected onto (001) and illustrating some of the hydrogen bonds involving the iodide ions (large circles) and the manner in which the cations are linked together *via* these bonds. The iodide ions are labeled with their fractional *z* coordinates and the urea molecules illustrated are labeled according to the fractional *z* coordinates of the titanium atoms to which they are coordinated.

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(20) A. Caron and J. Donohue, *Acta Cryst.*, **17**, 544 (1964).

(21) J. E. Worsham, H. A. Levy, and S. W. Peterson, *ibid.*, **10**, 319 (1957).

(22) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., and London, 1960, p 289.

(23) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(24) See for example C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 104.

(25) B. N. Figgis, *J. Chem. Soc.*, 4887 (1965).

present model, the latter is always the ground level. Moreover, the coefficients of the free-ion orbitals in the two sets of e orbitals differ from those for the octahedral e_g and $t_{2g}^{\pm}$ orbitals, a result which is also a feature of the D_{3d} distorted model but which has previously been neglected.[5,6]

The energy levels calculated for the explicit set of bond angles found for the $Ti(OC(NH_2)_2)_6^{3+}$ ion, *i.e.*, with the 5.6° "twist" away from an octahedron, are in terms of Dq: a_1, $-4Dq$; e(1), $-3.95Dq$; e(2), $5.95Dq$; or with $Dq = 1700\ cm^{-1}$: a_1, $-6800\ cm^{-1}$; e(1), $-6720\ cm^{-1}$; e(2), $10{,}120\ cm^{-1}$. The ground state for this geometry is therefore $^2A_1$, a result which at first sight is at variance with the single-crystal polarization measurements.[26] There is then a small splitting $\sim 100\ cm^{-1}$ of the t_{2g} set, but this, together with the change in "composition" of the e(1) orbitals, is sufficient to cause a marked change in magnetic properties from those calculated for the $^2T_{2g}$ term. A more complete discussion of the influence of this type of distortion for configurations other than d^1 and on the magnetic properties of this and other trigonally distorted molecules will be discussed in detail elsewhere.[19]

[26] R. Dingle, *J. Chem. Phys.*, **50**, 545 (1969).

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The Crystal and Molecular Structure of Ethanolatotetra-μ-thiobenzoato-dinickel(II), $[Ni(C_6H_5COS)_2]_2C_2H_5OH$

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A three-dimensional crystal structure analysis using 2483 counter-diffractometric measurements has been carried out for ethanolatotetra-μ-thiobenzoato-dinickel(II), $[Ni(C_6H_5COS)_2]_2C_2H_5OH$. The cell constants were $a = 10.44$ (2) Å, $b = 11.66$ (2) Å, $c = 12.69$ (2) Å, $\alpha = 91°\ 1'$, $\beta = 92°\ 55'$, $\gamma = 93°\ 0'$ (all $\pm 5'$), $d_m = 1.54$, $d_c = 1.535$ g/cm^3, space group $P\bar{1}$, and $Z = 2$. R, after least-squares refinement with individual isotropic thermal parameters, is 0.053. The two nickel atoms in the complex are bridged by the four thiobenzoate residues so that one metal atom is surrounded by four sulfur atoms in a square-planar fashion and the other by four oxygen atoms in a similar manner. The two planes are twisted about the Ni–Ni axis by some 23° from an eclipsed configuration. The fifth coordination site of the second nickel atom is occupied by the oxygen atom of the ethanol moiety. The Ni–S distances, 2.221–2.230 (5) Å, are characteristic of square-planar, low-spin complexes while the Ni–O distances, 2.010–2.058 (7) Å, are compatible with those found in high-spin complexes. It is concluded that the observed magnetic moment of the dimer, 2.40 BM/nickel(II) ion, arises from the presence of two unpaired electron spins on the nickel ion of C_{4v} symmetry and that, despite a Ni–Ni separation of only 2.503 (4) Å, the metal–metal interaction is probably quite weak. In the crystal the molecules are held together by weak axial Ni–S interactions, 2.814 (5) Å, between the dimers so as to form centrosymmetric tetramers. These are further linked together by weak O–H···O hydrogen bonds of length 2.86 Å involving the ethanol hydroxyl group as donor to an in-plane oxygen of a neighboring molecule.

Introduction

As part of a study of reactions between sulfur donor ligands and transition metal ions[1] we have synthesized nickel(II) compounds of the general formula $Ni(RCOS)_2 \cdot 0.5C_2H_5OH$, where R is CH_3, C_2H_5, or C_6H_5. These complexes show temperature-independent magnetic moments in the range 2.3–2.4 BM/nickel(II) ion. Measurement of the molecular weights of the compounds in chloroform solution suggests the presence of binuclear species. To establish the structure of these molecules a single-crystal X-ray diffraction study of the thiobenzoate complex, R = C_6H_5, has been carried out.

Measurement of Crystal and Intensity Data

Recrystallization of the complex from anhydrous ethanol gave fragile purple-red prisms with the bounding faces (100), (010), and (001) developed. The lattice parameters, measured at room temperature, were derived from 25° precession photographs taken with Zr-filtered Mo Kα radiation (λ 0.7107 Å) and are $a = 10.44$ Å, $b = 11.66$ Å, $c = 12.69$ Å, $\alpha = 91°\ 1'$, $\beta = 92°\ 55'$, and $\gamma = 93°\ 0'$. The errors in the cell edges may be taken as the 1 part in 600 commonly associated with the precession method and imposed by uncertainty in the centering of the crystal. In the measured angles the error is $\pm 5'$. The unit cell volume is 1540 Å^3 and the calculated density on the assumption of two dimeric units of formula $Ni_2C_{26}H_{30}O_5S_4$ per unit cell is 1.535 g/cm^3, in agreement with the value of 1.54 ± 0.01 g/cm^3 measured by pycnometry of an ethyl iodide–benzene mixture. $F(000) = 732$.

The possible triclinic space groups are P1 and $P\bar{1}$. No tests were made for pyroelectric or piezoelectric effects but with $Z = 2$ the centrosymmetric space group was chosen as the more likely, a choice justified by the outcome of the analysis. This space group requires no symmetry within the dimeric units but the association of these dimers into tetramers in the

[1] G. A. Melson, N. P. Crawford, and B. J. Geddes, *Inorg. Chem.*, **9**, 1123 (1970).