(10) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969.
(11) The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by the Picker Corp.
(12) T. C. Furnas, "Single Crystal Orienter Instruction Manual", General Electric Co., Milwaukee, Wis., 1957.
(13) S. Z. Goldberg, *Acta Crystallogr., Sect. B*, in press.
(14) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(15) All computations were carried out on an IBM 360/65 computer. Data reduction was performed with an extensively modified version of Raymond's URFACS. In addition, local versions of the following were used: Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plotting program.
(16) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; estimated standard deviation of an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o and N_v are the number of observations and variables, respectively.
(17) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(19) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(20) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965); *Acta Crystallogr.*, **18**, 511 (1965).
(21) Supplementary material.
(22) W. Hieber and K. Hienicke, *Z. Anorg. Allg. Chem.*, **305**, 316, 321 (1962).
(23) (a) M. C. Baird, *Inorg. Chim. Acta*, **5**, 54 (1971); (b) S. D. Robinson and M. F. Uttley, *J. Chem. Soc. A*, 1254 (1971).
(24) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).

Contribution from the Istituto di Strutturistica Chimica, Università di Parma,
Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., 43100 Parma, Italy, from the
Istituto di Chimica Analitica, Università di Pisa, 56100 Pisa, Italy, and from the Istituto
di Tecnologie Chimiche Speciali, Facoltà di Chimica Industriale, Università di Bologna, 40136 Bologna, Italy

Spectroscopic Properties and Crystal Structure Analysis of an Intermediate in the Reaction of Bis(oxalato)platinate(II) with Thiocyanate: Potassium Bis(oxalato)bis(thiocyanato)platinate(II) Tetrahydrate

A. CHIESI VILLA,*[1a] A. GAETANI MANFREDOTTI,[1a] A. GIACOMELLI,[1b] C. GUASTINI,[1a] and A. INDELLI[1c]

Received November 13, 1974 AIC40775V

Potassium bis(oxalato)bis(thiocyanato)platinate(II) tetrahydrate, $K_4[Pt(C_2O_4)_2(SCN)_2]\cdot 4H_2O$, has been obtained as intermediate in the reaction of bis(oxalato)platinate(II) with potassium thiocyanate. Its structure has been determined from three-dimensional X-ray data collected by counter methods using the θ–2θ technique. The complex crystallizes in the triclinic space group $P\bar{1}$ with a = 11.04 (1), b = 7.14 (1), c = 6.66 (1) Å; α = 108.6 (1), β = 90.3 (1), γ = 101.1 (1)°. Observed and calculated densities are 2.40 and 2.38 g cm^{-3}, respectively, for mol wt 715.9 and Z = 1. The structure was solved by the standard heavy-atom technique and refined by least squares to a conventional R factor of 0.049. The unidentate character of the oxalate ion in this compound has been confirmed. Coordination around platinum is square planar and involves two thiocyanate groups and two oxalate ions (Pt–S = 2.329 (4) and Pt–O(1) = 2.015 (6) Å). Ir and NMR experiments prove that the tendency to be associated with the crystal is greater for H_2O than for D_2O.

Introduction

In a preceding paper[2] on the rate of the reaction between bis(oxalato)platinate(II) and thiocyanate, an intermediate product was isolated which contained two oxalate and two thiocyanate groups per atom of platinum. This was considered evidence that the first step of the substitution reaction involves oxalate groups which act as unidentate ligands. Such intermediates have been postulated many times in substitution reactions of oxalato complexes as well in racemization and exchange reactions.[3] However, as far as we know, no coordination compounds with unidentate oxalate had been previously isolated. We succeeded in recrystallizing the intermediate without decomposition and in obtaining crystals large enough for X-ray analysis. We proceeded therefore to a more accurate investigation of this compound.

Experimental Section

Preparation. A mixture of 0.02 M $K_2Pt(C_2O_4)_2$ and 0.1 M KSCN was allowed to react at 45° under spectrophotometric control. When the optical density reached a minimum, 3 volumes of cooled acetone were added and the mixture was quickly cooled to 0°. The precipitate was filtered, washed with acetone, and dissolved in the minimum amount of water at room temperature. By slow addition of acetone gold-yellow prismatic crystals suitable for a single-crystal X-ray analysis could be obtained in about 6 hr. The ir spectra in Nujol and Tripen (poly(chlorotrifluoroethylene) oil) were the same as with the original precipitate.[2]

X-Ray Data. The unit cell dimensions, determined from rotation and Weissenberg photographs and refined by an "on-line" single-crystal automated Siemens diffractometer, are as follows, for $K_4[Pt(C_2O_4)_2(SCN)_2]\cdot 4H_2O$, fw = 715.9: a 11.04 (1), b = 7.14 (1), c = 6.66 (1) Å; α = 108.6 (1), β = 90.3 (1), γ = 101.1 (1)°; V = 487.0 Å^3; d_{measd} = 2.40 g cm^{-3} (by flotation); Z = 1; d_{calcd} = 2.38 g cm^{-3}, $F(000)$ = 340; μ = 86.7 cm^{-1} (Mo Kα); triclinic, space group $P\bar{1}$ (from structural analysis).

Three-dimensional intensity data were taken at room temperature from a prismatic crystal of length 0.21 mm and of cross section measuring 0.09 mm × 0.11 mm mounted with c along the ϕ axis of the Siemens diffractometer. Niobium-filtered Mo Kα radiation at a takeoff angle of 4° was employed. The pulse height discriminator was set to accept 90% of the Mo K$\bar{\alpha}$ peak. The moving counter–moving crystal scan technique was used with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min).

The 120 reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. For intensities and background the "five-points technique"[4] was used. A total of 2600 independent reflections were measured and 2563 were used in the crystal analysis considering the reflections whose intensities were less than twice their standard deviations ($\sigma^2(I)$ = total counts + (0.01 × intensity)^2) as being unobserved.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by successive comparison with the calculated values. No correction for absorption was applied ($\mu\bar{r}$ = 0.4) and therefore the thermal coefficients given in Table I are influenced by this omission.

Solution and Refinement of the Structure. The structure was solved considering all the structure factors to be positive; this implied the assumption of the space group $P\bar{1}$ with the Pt atom at the origin. The Fourier map confirmed this assumption revealing all nonhydrogen atoms and the presence of four water molecules instead of the three suggested in the previous paper.[2]

The refinement was carried out by means of block-diagonal least squares, isotropically down to R = 15.1% and anisotropically down to R = 5.0% ($R = \sum||F_o| - |F_c||/\sum|F_o|$). The lack of corrections for absorption and anomalous scattering resulted in data which do not

Table I. Fractional Atomic Coordinates,[a] Thermal Parameters,[b] and Esd's in Parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0	0	0	117 (1)	285 (1)	152 (1)	113 (1)	0 (1)	43 (1)
K(1)	4499 (1)	−2419 (3)	−4056 (3)	187 (5)	372 (6)	234 (5)	93 (4)	15 (4)	91 (4)
K(2)	1913 (2)	1014 (3)	−4511 (3)	194 (5)	409 (7)	231 (5)	110 (5)	29 (4)	72 (5)
S	1023 (2)	3306 (3)	506 (3)	220 (6)	315 (6)	302 (7)	110 (5)	−30 (5)	101 (5)
O(1)	1469 (4)	−761 (8)	1113 (8)	123 (14)	379 (19)	211 (16)	148 (13)	0 (13)	87 (14)
O(2)	2315 (6)	−1591 (11)	−2050 (9)	297 (25)	650 (33)	226 (22)	272 (24)	40 (19)	153 (22)
O(3)	3528 (5)	−942 (8)	3054 (9)	253 (20)	369 (21)	244 (19)	187 (16)	−23 (16)	67 (16)
O(4)	4161 (6)	−2554 (9)	−66 (9)	329 (23)	456 (25)	223 (19)	301 (20)	31 (17)	74 (17)
$O_w(1)$	4064 (5)	3305 (9)	−2370 (9)	240 (20)	445 (24)	228 (19)	159 (18)	−1 (16)	82 (17)
$O_w(2)$	−180 (7)	2693 (11)	−4665 (11)	413 (30)	517 (30)	353 (27)	215 (25)	41 (23)	140 (24)
N	3183 (8)	3780 (13)	3027 (14)	289 (29)	506 (36)	402 (34)	11 (26)	−103 (26)	169 (28)
C(1)	2293 (7)	3581 (11)	2011 (12)	218 (25)	285 (24)	293 (27)	9 (20)	−2 (21)	85 (21)
C(2)	2330 (6)	−1304 (9)	−76 (10)	191 (21)	284 (22)	167 (20)	160 (18)	1 (16)	29 (17)
C(3)	3437 (5)	−1636 (9)	1102 (10)	123 (19)	277 (21)	220 (22)	83 (16)	−2 (16)	70 (18)
H(51)	400	450	−148						
H(52)	468	274	−153						

[a] The listed coordinates are multiplied by 10^4 for nonhydrogen atoms and by 10^3 for hydrogen atoms. [b] The listed B_{ij}'s are in Å^2 and are multiplied by 10^2. The anisotropic temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The isotropic temperature factor $B = 4.0$ Å^2 was assigned to hydrogen atoms.

Table II. Interatomic Distances (Å) and Angles (deg)

(a) In the $[Pt(C_2O_4)_2(SCN)_2]^{2-}$ Ion

Pt–S	2.329 (4)	S–Pt–O(1)	94.0 (2)
Pt–O(1)	2.015 (6)	S–C(1)–N	178.9 (8)
S–C(1)	1.662 (9)	Pt–S–C(1)	103.8 (3)
C(1)–N	1.150 (12)	Pt–O(1)–C(2)	121.4 (4)
C(2)–O(1)	1.279 (8)	O(1)–C(2)–O(2)	125.3 (7)
C(2)–O(2)	1.264 (9)	O(1)–C(2)–C(3)	114.1 (5)
C(3)–O(3)	1.231 (9)	O(2)–C(2)–C(3)	120.7 (6)
C(3)–O(4)	1.248 (9)	O(3)–C(3)–O(4)	127.3 (6)
C(2)–C(3)	1.545 (10)	C(2)–C(3)–O(3)	117.5 (6)
		C(2)–C(3)–O(4)	115.2 (6)

(b) In the Potassium Coordination Spheres[a]

K(1)–O(2)	2.833 (8)	K(2)–O(2)	2.932 (9)
K(1)–O(4)	2.715 (8)	K(2)–O_w(1)	2.707 (7)
K(1)–N^{i}	2.888 (9)	K(2)–O_w(2)	2.816 (9)
K(1)–O(3)^{ii}	2.770 (6)	K(2)–O(1)^{ii}	2.780 (5)
K(1)–O(3)^{iv}	2.811 (6)	K(2)–O(3)^{ii}	2.703 (6)
K(1)–O_w(1)^{iii}	2.837 (6)	K(2)–O_w(2)^{v}	2.843 (8)
K(1)–N^{iv}	3.054 (9)	K(2)–N^{ii}	3.095 (10)

(c) Hydrogen Bonds[a]

O_w(1)–H···O(4)^{iv}	2.772 (9)	O_w(1)–H(52)–O(4)^{iv}	164
O_w(1)–H···O(4)^{vi}	2.844 (9)	O_w(1)–H(51)–O(4)^{vi}	164

[a] i = $x, y - 1, z - 1$; ii = $x, y, z - 1$; iii = $1 - x, \bar{y}, \bar{z} - 1$; iv = $1 - x, \bar{y}, \bar{z}$; v = $\bar{x}, \bar{y}, \bar{z} - 1$; vi = $x, 1 + y, z$.

yield an improved fit. A subsequent difference Fourier revealed a peak of 4.5 e Å^{-3} at ca. 1 Å from platinum on the line Pt–S. No other peak exceeded 1.6 e Å^{-3}. The presence of these peaks, to which a real physical meaning cannot be attributed, made impossible the direct location of hydrogen atoms. Only for those attached to O_w(1), could the probable position be inferred considering the hydrogen-bonding interactions in which they were involved. These positions correspond to residual electron densities of 1.4 and 1.3 e Å^{-3}. These atoms were included in the structure factor calculations with isotropic thermal parameters of 4.0 Å^2 in the subsequent refinements but were not themselves refined.

The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$ with unit weights up to $R = 5.0\%$. Only a small improvement down to $R = 4.9\%$ was obtained by applying in three further cycles of refinement the weighting scheme proposed by Cruickshank:[5] $w^{-1} = A + B|F_o| + C|F_o|^2$ ($A = 0.09151$, $B = 0.03343$, $C = 0.003053$ deduced from the $\langle|\Delta F|\rangle$ vs. $|F|$ distribution[6]).

In the last stage of the refinement no parameter shifted by more than 0.3 times its estimated standard deviation and the refinement was considered to have converged at $R = 4.9\%$. No evidence for secondary extinction was found. The atomic scattering factors were those of Cromer and Mann[7] for Pt, K, S, O, N, and C and those of Stewart, Davidson, and Simpson[8] for H. All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, Italy, using programs of Immirzi.[9] A table of observed and calculated structure factor amplitudes is included with the supplementary material. The final atomic positional and thermal parameters are listed in Table I.

Deuterium Exchange. The precipitate was dissolved in 99.8% D_2O and precipitated with anhydrous acetone or repeatedly dissolved in D_2O and dried under vacuum over P_2O_5. In all cases, although the KBr windows were accurately dried and the Tripen used for the mull did not reveal ir absorption due to H_2O, absorption bands in the 3200–3600-cm^{-1} region were observed and were actually stronger than the bands in the 2300–2700-cm^{-1} region, which are due to deuterium. Another sample of crystals was prepared starting from solutions in 99.8% D_2O and using only anhydrous acetone. Even this sample showed very weak bands in the 3200–3600-cm^{-1} region. By dissolving the deuterated product in 90% D_2O and drying on P_2O_5 under vacuum, the bands due to H were almost as strong as those due to D. By dissolving the product in water and drying, the bands of D disappeared.

An NMR Measurement. A sample of the crystals was dissolved in 99.8% D_2O and its NMR spectrum was taken using a Varian S-60T spectrometer. A single peak due to H_2O was observed. By comparison with an internal standard of 2,2,3,3-tetradeuteriotrimethylsilylpropionic acid, sodium salt, the content of water was determined to be 10.8% (theoretical 10.1%), in substancial agreement with TGA analysis. Samples repeatedly dissolved in 99.8% D_2O and crystallized by drying on P_2O_5 under vacuum, when redissolved in 99.8% D_2O, gave water contents ranging from 5.6 to 3.7% without any clear trend toward a decrease when increasing the number of recrystallizations. Some degree of decomposition was noticed after three recrystallizations. These results are in qualitative agreement with the deuterium-exchange experiments performed by ir spectroscopy.

TGA and DTA Analysis. A loss of weight of 10.56% was observed around 150° and a further one of 8.0% around 230°. By DTA an endothermic event was observed around 150° and an exothermic one around 230°. Using a larger resolution it appears that the first endothermal reaction occurs in two steps. At higher temperatures there is another endothermal reaction with a very broad peak around 380°, which indicates extensive decomposition.

Results and Discussion

Interatomic distances and angles with their estimated standard deviations (esd's) are collected in Table II. Important least-squares planes are given in Table III.

The projection of the structure on (001) with the atomic numbering scheme is shown in Figure 1 and the overall environments of the two potassium ions are illustrated in Figure 2.

The unidentate character of the oxalate group is clearly evident from Figure 1, which shows that the coordination around platinum is square planar and involves two sulfur atoms from the thiocyanate groups (Pt–S = 2.329 (4) Å) and two oxygen atoms from two oxalate ions (Pt–O(1) = 2.015 (6) Å) as suggested in the previous paper.[2]

The Pt^{II}–S and Pt^{II}–O distances fall in the ranges of the values usually found, i.e., 2.27–2.41 Å for Pt–S (e.g., 2.284 (7)–2.308 (7) Å in bis(ethylene-1,2-dithiolene)platinum;[10]

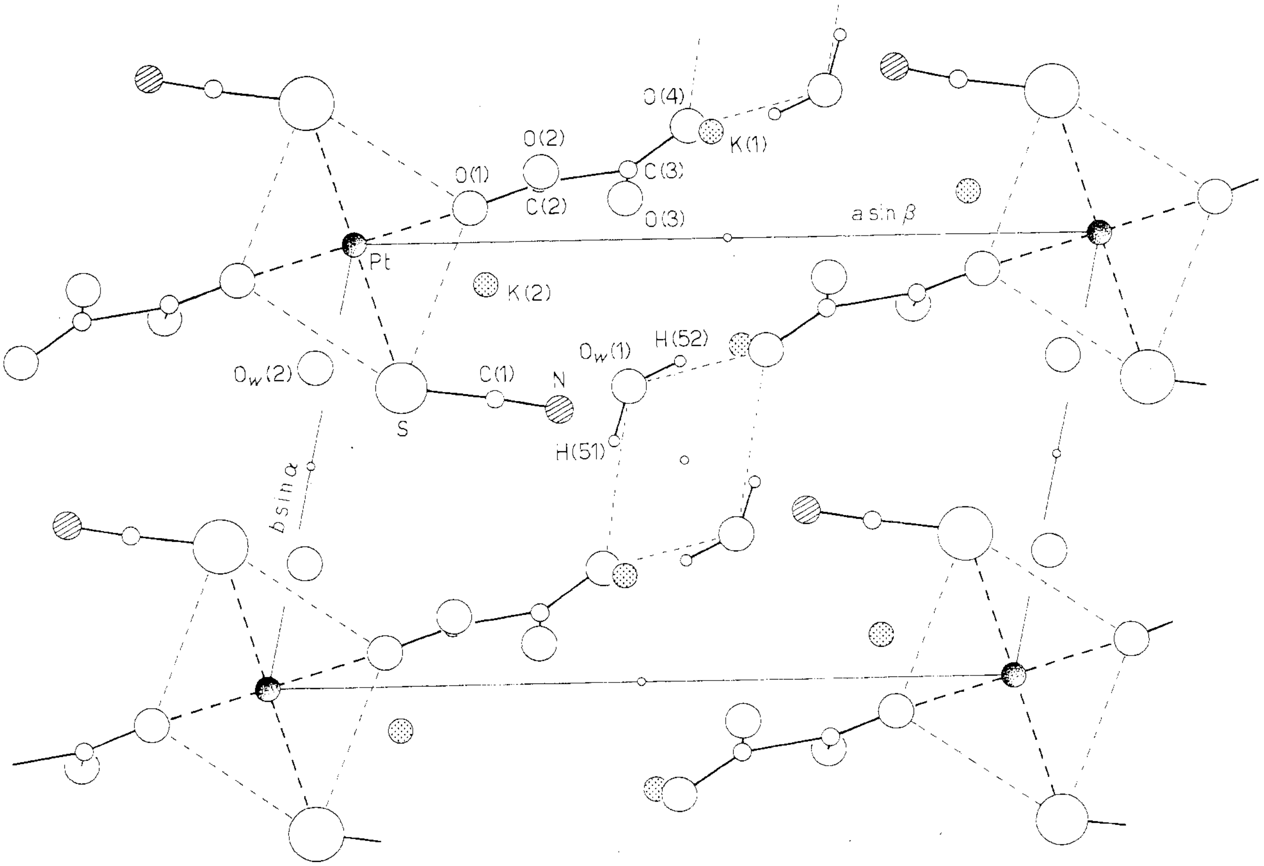

Figure 1. Projection of the structure on (001).

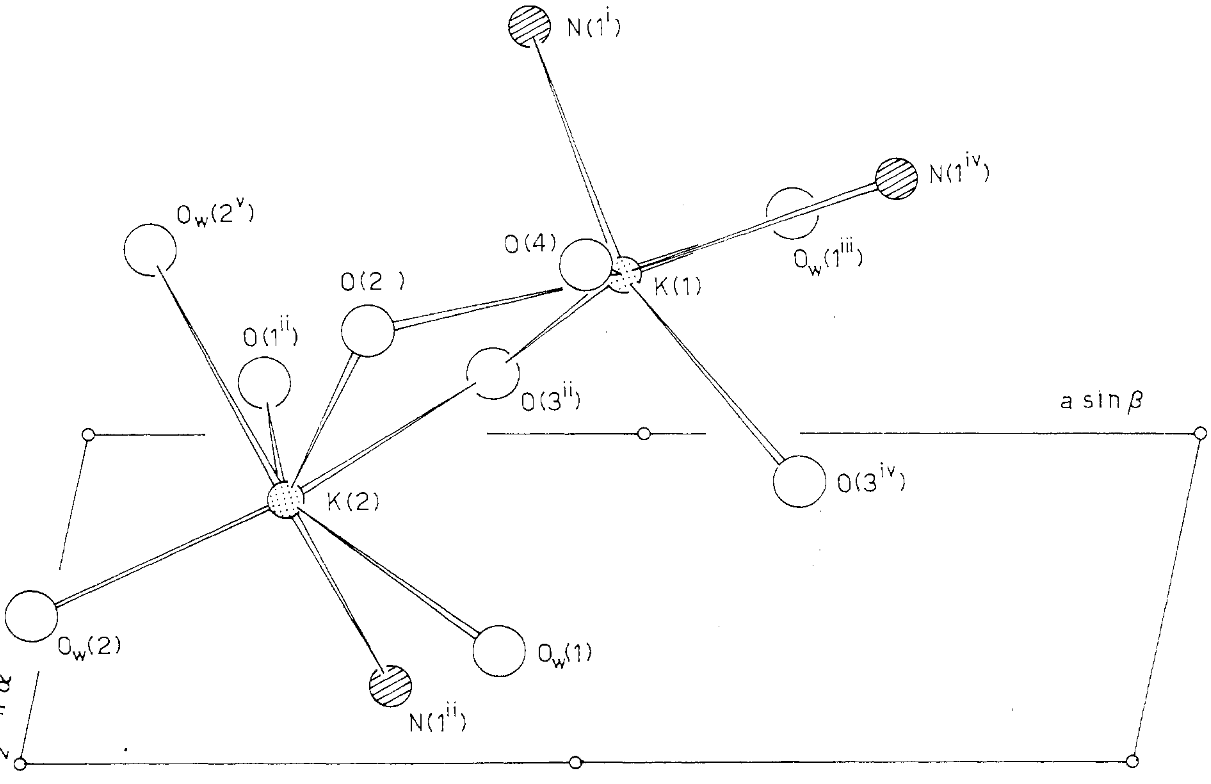

Figure 2. Projection of the potassium environments on (001).

2.267 (6)–2.378 (6) Å in dichlorobis-μ-ethanethiolato-bis(tripropylphosphine)diplatinum(II);[11] 2.322 (4) and 2.340 (5) Å in [Pt(S$_2$CF)(PPh$_3$)$_2$][HF]$_2$;[12] 2.374 (8) Å in *cis*-thiocyanatoisothiocyanatobis(3,3-dimethylbutynyldiphenylphosphine)platinum(II);[13] 2.327 (5) and 2.408 (4) Å, respectively, in α and β isomers of dichlorobis-μ-thiocyanato-bis(tri-*n*-propylphosphine)platinum(II)[14]) and 1.96–2.09 Å for Pt–O (e.g., 2.00 (1) Å in potassium bis(oxalato)platinate(II) dihydrate;[15] 1.968 (14) and 2.072 (14) Å in potassium bis(acetylacetonato)chloroplatinate(II);[16] 2.016 (5) Å in bis-

Table III. Equations of Least-Squares Planes and Distances (Å) from These Planes[a]

(a) Plane Containing Pt, S, O(1)
Equation: $0.3791X - 0.0576Y - 0.9236Z = 0$

(b) Plane Containing O(1), O(2), C(2), C(3), O(3), O(4)
Equation: $0.4751X + 0.8773Y + 0.0679Z + 0.0588 = 0$

O(1)	0.119	C(3)	0.020
O(2)	−0.161	O(3)	−0.123
C(2)	−0.020	O(4)	0.164

(c) Plane containing O(1), O(2), C(2), C(3)
Equation: $0.4314X + 0.8829Y + 0.1856Z + 0.1680 = 0$

O(1)	0.001	C(2)	−0.005
O(2)	0.002	C(3)	0.001

(d) Plane Containing O(3), O(4), C(2), C(3)
Equation: $0.5434X + 0.8386Y - 0.0374Z - 0.1904 = 0$

O(3)	0.003	C(2)	0.003
O(4)	0.003	C(3)	−0.009

[a] Planes are defined as $C_1X + C_2Y + C_3Z + d = 0$, where X, Y, Z are cartesian coordinates obtained from the triclinic coordinates x, y, z by the matrix

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{pmatrix}$$

(triphenylphosphine)(dibenzoylhydrazido)platinum;[17] 2.007 (21)–2.091 (18) Å in *cyclo*-bis(μ-acetato-μ-nitrosyl)-bis-[di-μ-acetato-diplatinum(II)][18]). Nevertheless the significance of such a rough comparison is doubtful, as these distances are particularly influenced both by trans and π effects. So the comparison must be restricted only to those compounds where the bonding situation is similar. By assuming the trans effect of sulfur is not much different from that of chlorine, a comparison can be made with the α isomer of dichlorodi-μ-thiocyanato-bis(tri-*n*-propylphosphine)platinum(II)[14] where sulfur is trans to chlorine and the Pt–S distance is 2.327 (5) Å, in quite good agreement with that found in the present analysis. This distance compares well also with that of PtS (2.312 Å).[19] The Pt–O distance is not significantly different from those observed in potassium bis(oxalato)platinate(II) dihydrate (2.00 (1) Å).[15]

The oxalate group is not planar (the torsional angle around C(2)–C(3) is 13°) and is oriented in such a way that its mean plane forms an angle of 86° with respect to the coordination plane. The C–O distances are not significantly different, the double bond being delocalized in each carboxy group as normally found in complexes containing ionized carboxy groups.

A comparison of this oxalate geometry with that of potassium oxalate[20,21] shows that the differences are not significant as a consequence of the comparatively high values of the esd's in the present analysis. On the contrary a significant difference is observed in the conformation of the ion, which is centrosymmetric with a small shifting from the complete planarity in potassium oxalate and is twisted around C–C in the present compound. This twisting can be accounted for by the asymmetry of the interactions involving the terminal oxygens. The ir data and their discussion have been published in the preceding paper.[2] It can be added that the difference in frequency between asymmetrical and symmetrical C–O stretching bands is here about the same as in the free oxalate ion or slightly smaller (210 in comparison with 222 cm^{-1}). For carbonates and nitrates the following sequence is observed for $\nu_{asym} - \nu_{sym}$: basic salt < monodentate ligand < bidentate ligand < acid < organic esters.[23] Essentially the same sequence is observed for the oxalates, but with a possible inversion at the beginning of the sequence. This can be related, perhaps, to the twisting of the ligand observed in the monodentate oxalate.

The number of water molecules for every platinum ion is 4 instead of 3 as provisionally suggested in the preceding paper;[2] of these, two are hydrogen bonded to the free ends of the COO groups linking in chains the coordination polyhedra, and the other two only interact with the potassium ions, which show heptacoordination (Figure 2) and play an important role in determining packing. These two water molecules are 3.487 (7) Å from the Pt in the octahedral positions (the angle between the Pt···O$_w$(2) direction and the coordination plane is 72°), but it is doubtful that these long contacts correspond to bond interactions.

The presence of four water molecules is also shown by TGA (loss of weight: calculated, 10.1%; found, 10.56%), and DTA indicates that they are not equivalent as found from the crystal structure analysis. The shape of the peak is typical of crystallization water. In the preceding paper[2] in the absence of TGA equipment it was impossible to determine the exact water content, because in the long time required to dry the substance at 120° some decomposition occurred. This was revealed by the fact that the ir peak at 2110 cm^{-1} was split into two peaks at 2115 and 2170 cm^{-1}. The supposed hexacoordination of Pt(II) with two water molecules above and below the square coordination plane is disproved by the present experiments, so a coordinative interaction between H_2O and Pt cannot be considered responsible for the incomplete exchange with D_2O. On the other hand this exchange does not exceed ~50% in spite of the repeated treatments with D_2O, as shown by ir and NMR experiments. Probably the exchanged H_2O molecules are those not involved in hydrogen bondings which seem to maintain, in D_2O solution, a structural situation similar to that found in the crystal state. A greater tendency of H_2O in comparison with D_2O to be associated with ions in crystals has been found by Barrer and Denny,[22] although to a much smaller extent than in our case. It should be noticed, however, that in the spectrum of deuterated $K_4[(ox)_2Co(OH)_2Co(ox)_2]$, published by Nakamoto,[23] the stretching band of OH at 3500 cm^{-1} is clearly visible, although the bending band Co–O–H at 1100 cm^{-1} has disappeared.

Acknowledgment. The authors thank Mr. M. Nebuloni (Laboratori Ricerche Gruppo Lepetit S.P.A., Milan, Italy) for TGA and DTA analyses and Professors L. Cavalca and M. Nardelli for useful discussion. A. Giacomelli and A. Indelli thank the Consiglio Nazionale delle Ricerche, Rome, Italy, for financial support.

Registry No. $K_2Pt(C_2O_4)_2$, 35371-78-9; KSCN, 333-20-0; $K_4[Pt(C_2O_4)_2(SCN)_2]\cdot 4H_2O$, 54852-39-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40775V.

References and Notes

(1) (a) University of Parma. (b) University of Pisa. (c) University of Bologna.
(2) A. Giacomelli and A. Indelli, *Inorg. Chem.*, **11**, 1033 (1972).
(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", New York, N.Y., 1967, Chapter 4, pp 300–328.
(4) W. Hoppe, *Acta Crystallogr., Sect. A*, **25**, 67 (1969).
(5) D. W. J. Cruickshank, "Computing Methods in Crystallography", J. S. Rollett, London, 1965, Chapter 14.
(6) G. H. Stout and L. H. Jensen, "X-ray Structure Determination", Macmillan, New York, N.Y., 1968, p 455.
(7) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(9) A. Immirzi, *Ric. Sci.*, **37**, 743 (1967).
(10) K. W. Browell, T. Bursh, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972).

(11) M. C. Hall, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc., Dalton Trans.*, 1544 (1972).
(12) J. A. Evans, M. J. Hacker, R. D. W. Kemmit, D. R. Russell, and J. Stocks, *J. Chem. Soc., Chem. Commun.*, 72 (1972).
(13) Y. S. Wong, S. Jacobson, P. C. Chieh, and A. J. Carty, *Inorg. Chem.*, **13**, 284 (1974).
(14) U. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc. A*, 2770 (1970).
(15) R. Mattes and K. Krogmann, *Z. Anorg. Allg. Chem.*, **332**, 247 (1964).
(16) R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc. A*, 485 (1969).
(17) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, **12**, 2290 (1973).
(18) P. de Meester and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1194 (1973).
(19) F. Gronvold, H. Haraldsen, and A. Kjekshus, *Acta Chem. Scand.*, **14**, 1879 (1960).
(20) D. J. Hodgson and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 469 (1969).
(21) A. Sequeira, S. Srikanta, and R. Chidambaram, *Acta Crystallogr., Sect. B*, **26**, 77 (1970).
(22) R. M. Barrer and A. F. Denny, *J. Chem. Soc. A*, 4677 (1964).
(23) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1970, pp 169–173.

Contribution from the Research School of Chemistry,
The Australian National University, Canberra, A.C.T. 2600, Australia

Crystal Structure of Δ-*R*-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}alaO)]I_2$ and Related Strain Energy Minimization Calculations

B. F. ANDERSON, D. A. BUCKINGHAM,* G. J. GAINSFORD, G. B. ROBERTSON, and A. M. SARGESON

Received November 25, 1974 AIC40803+

The absolute configuration of Δ-*R*-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}alaO)]I_2$ has been determined by X-ray methods ($P4_1$, $a = b = 8.878$ Å, $c = 21.398$ Å, $Z = 4$, $R_1 = 5.2\%$, $R_2 = 5.5\%$ (for 1472 unique data with $I \geq 3\sigma(I)$); the amino acid contains trans methyl groups with the *R* and *S* configurations about the N and C centers, respectively; the ethylenediamine chelates adopt δ and λ conformations. Strain energy minimization calculations predict the stability order Δ-*S*(*R*), Δ-*R*(*S*), Δ-*S*(*S*), Δ-*R*(*R*) and correctly predict the energy difference between the Δ-*S*(*R*) and Δ-*R*(*S*) isomers (observed 1.0 kcal mol^{-1}; calculated 0.8). The structure of the energy-minimized and crystal Δ-*R*(*S*) cations agree closely. Similar agreement is found between the calculated and observed structures of the Δ-*S*-$[Co(en)_2(sar)]^{2+}$ (sar = sarcosinato) cation. Calculations predict the stability order *S*(*R*), *S*(*S*), *R*(*S*), *R*(*R*) for the Δ-β_2-*RR*-$[Co(trien)(N\text{-}Me\text{-}alaO)]^{2+}$ cation and the three isolated isomers[6] are assigned. Structures and relative energies of the configurational isomers of Δ-β_2-$[Co(trien)(sar)]^{2+}$ are discussed.

Introduction

In a recent study of the Δ-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}alaO)]^{2+}$ ion[1] (en = ethylenediamine, *N*-Me-(*S*)-alaO = *N*-methyl-(*S*)-alaninato anion) it was shown that at pH >12 mutarotation about the C center of the alaninato chelate occurred and that at equilibrium the Δ-*R*:Δ-*S* ratio was ca. 4. No mutarotation was observed for either isomer in more neutral solutions, pH <7, and it was concluded that the stereochemistry about the alaninato *N*-methyl center was controlled by the adjacent chiral metal and carbon centers in both ions. However, whereas in the Δ-*R* cation this leads to the stereospecific trans arrangement of the methyl groups, in the Δ-*S* species two alternatives are possible: the trans configuration which involves considerable strain in an adjacent ethylenediamine ring but avoids intramethyl group interactions and the cis configuration where the reverse situation obtains. Previous experience with the $[Co(en)_2(sar)]^{2+}$,[2] β_2-$[Co(trien)(sar)]^{2+}$,[3] β_2-$[Co(trien)(pro)^{2+}]$,[4,5] and $[Co(trien)(N\text{-}Me\text{-}(S)\text{-}alaO)]^{2+}$ [6] ions and an examination of molecular models suggested that chelate ring–methyl group interactions would dominate the issue and predicted that a cis arrangement would occur in the minor Δ-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}alaO)]^{2+}$ component. However, strain energy calculations predicted that the trans structure would be stabilized in the Δ-*S* ion. It was therefore of some importance to determine the structure and this paper describes these results.

The agreement found between the X-ray and strain energy minimized structures for the Δ-*R*-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}alaO)]^{2+}$ ion (vide infra) prompted us to reexamine our results for the Δ-β_2-$[Co(trien)(N\text{-}Me\text{-}(S)\text{-}alaO)]^{2+}$,[6] Δ-$[Co(en)_2(sar)]^{2+}$,[2] and Δ-$\beta_2$-$[Co(trien)(sar)]^{2+}$ [3] ions. These data are briefly discussed at the end of the paper.

Experimental Section

A. Crystallography and Data Collection for Δ-*R*-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}alaO)]I_2$. The complex crystallized from water as deep red distorted octahedra.[1] Preliminary cell dimensions and the space group were determined from precession photographs and the final parameters and diffractometer orientation matrix refined by least-squares procedures[7] from the setting angles of 12 high-angle reflections measured on a Picker FACS-1 four-circle diffractometer.

Cell data:[8] $CoI_2C_8N_5O_2H_{24}$, mol wt 535.1, space group $P4_1$ ($00l$ reflections absent for $l \neq 4n$), $a = b = 8.8784$ (4) Å, $c = 21.3982$ (13) Å, $V = 1686.7$ Å^3, $Z = 4$, $d_c = 2.11$ g cm^{-3}, d_m(by flotation) = 2.12 g cm^{-3}, $\lambda(Cu\ K\alpha_1) = 1.54051$ Å, $\mu = 423.6$ cm^{-1}, $F(000) = 258$.

Cell parameters and all reflection data were collected from a typical crystal bounded by the eight faces of the [101] form and having dimensions 0.023 × 0.016 × 0.016 cm^3, parallel to *a*, *b*, and *c* respectively. It was mounted with the *a* axis parallel to the φ axis of the diffractometer system. Diffraction data for $3° \leq 2\theta \leq 126°$ were collected at room temperature (20 ± 1°) using graphite-monochromated Cu Kα radiation ($\bar{\lambda} = 1.5418$ Å) with a tube takeoff angle of 3°. Intensity measurements were made using the θ–2θ scan technique, scanning at a rate of 2°/min from 1° below the calculated position of the Cu $K\alpha_1$ maximum to 1° above that for Cu $K\alpha_2$. Backgrounds were counted for 10 sec at both ends of the scan range. Three moderately high-angle reflections, monitored after every 40 reflections, each showed a time-dependent decrease of about 13% in intensity over the period of data collection. The time dependence of the intensity decrease was corrected during data reduction by applying scale factors calculated from the three standards to each block of 40 reflections. This procedure assumes the intensity decrease to be independent of the scattering angle. Absorption corrections using a numerical integration method[9] over a grid of 10 × 10 × 12 points set parallel to *a*, *b*, and *c*, respectively, were applied. Transmission coefficients varied from 0.3 to 0.12.

A total of 2234 reflections were measured and corrected for Lorentz and polarization effects in the usual manner.[10] After sorting and merging equivalent reflections, 1472 unique data remained with $I \geq 3\sigma(I)$[11] and these were used for the structure refinement.

B. Structure Solution. The heavy-atom positions were determined from an unsharpened Patterson synthesis and the initial positions of all the nonhydrogen atoms were obtained from the first heavy-atom Fourier map. Refinement by full-matrix methods, with the *z* coordinate of I(1) fixed and by using anisotropic thermal parameters