Anomalous Scattering by Cobalt and Chlorine and Crystal Structure of (+)-Tris(ethylenediamine)cobalt(III) Chloride (+)-Tartrate Pentahydrate

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Abstract

Crystals of $[Co(C_2H_8N_2)_3]^{3+}.C_4H_4O_6^{2-}.Cl^-.5H_2O$, are triclinic, space group $P\bar{1}$ with $a = 8.261$ (3), $b = 8.507$ (3), $c = 8.149$ (3) Å, $\alpha = 101.20$ (1), $\beta = 95.27$ (1), $\gamma = 102.31$ (1)°, $Z = 1$. The structure and absolute configuration, A for (+)-Co(en)$_3$, were determined with 7688 observed reflections (Mo $K\alpha$ radiation) refined to $R = 0.022$. All H-atom positions were refined. These data and 3198 reflections measured with Cu $K\alpha$ radiation ($R = 0.029$) were used to determine anomalous-scattering terms. At Mo $K\alpha$, $f''(Co) = 0.962$ (10); $f''(Cl) = 0.155$ (10). At Cu $K\alpha$, f', $f''(Co) = -2.36$ (2), 3.92 (2); f', $f''(Cl) = 0.23$ (2), 0.72 (2) electrons.

Werner (1912) demonstrated the optical activity and octahedral nature of complexes of cobalt and ethylenediamine by using the crystallization of (+)-tartrate salts to separate the enantiomers. One of the salts he isolated was (+)-tris(ethylenediamine)cobalt(III) chloride (+)-tartrate pentahydrate. We first became interested in this material when it was the subject of an experiment devised by McClain (1972) for the elementary chemistry laboratory course at Berkeley. We determined the crystal structure because lack of knowledge of it was an embarrassment in explanations to students. Later we realized that this salt is suitable for measuring anomalous-scattering effects of cobalt and chlorine by a method described by Templeton & Templeton (1978).

In this paper we report the crystal structure and some measurements of scattering of Mo $K\alpha$ and Cu $K\alpha$ radiation. This study provides a foundation for some similar experiments with synchrotron radiation near the Co K absorption edge which will be described elsewhere.

Experimental

Crystals provided by Professor McClain had been prepared by air oxidation of an aqueous solution of ethylenediamine, HCl, and CoSO$_4$ in the presence of activated charcoal, followed by reaction with solid barium tartrate on a steam bath, concentration by boiling, and then cooling. Recrystallization from water yielded excellent orange-brown crystals for diffraction study. A crystal with dimensions $0.16 \times 0.28 \times 0.20$ mm was used for measurements with a Picker FACS-I diffractometer equipped with a graphite monochromator and Mo radiation ($\lambda = 0.70926$ Å for $K\alpha_1$). Cell dimensions were derived by least squares from the setting angles of 12 reflections ($50° < 2\theta < 55°$). Diffraction intensities were measured by the θ–2θ scan technique at $1°$ min^{-1} for 2θ, for all reflections in the full sphere up to $2\theta = 65°$ or $d = 0.66$ Å. The scan width was $1.2°$ in 2θ plus the α_1–α_2 splitting. Background was counted for 4 s at $0.5°$ past each end of the scan. Three reflections (600, 060, and 006) checked at intervals of 200 measurements indicated a uniform decrease in intensity of about 10% during 2.5 weeks of data collection, and each measurement was adjusted accordingly. An absorption correction ($\mu = 1.01$ mm^{-1}) was made using the program *HORSE* (Hamilton, 1969) that approximates the crystal as an array of points (480 in this case). The extreme correction factors were 1.15 and 1.22. Before the final refinement each structure factor was multiplied by $1.0 + 1.8 \times 10^{-7}I$, an empirical correction for extinction which was 1.18 for the strongest reflection, $\bar{1}11$; I is the uncorrected observed intensity.

For 188 reflections the intensity was less than σ estimated from counting statistics, and these were given zero weight in the structure refinement. The remaining 7688 reflections, including both members of each Bijvoet pair, were assigned weights $w = [\sigma(F)]^{-2}$; $\sigma(F)$ was derived from $\sigma(F^2) = [S^2 + (pF^2)^2]^{1/2}$, where S^2 is the variance due to counting statistics and $p = 0.03$.

Another crystal, $0.102 \times 0.084 \times 0.110$ mm, was used to measure diffraction intensities with Cu $K\alpha$ radiation. The technique was similar except that scan widths were $1.5°$, plus α_1–α_2 splitting, the scan speed was $2°$ min^{-1}, and backgrounds were measured at each end of the scan. Measurements of 3434 reflections, including both members of each Bijvoet pair, yielded

3198 with intensities greater than 3σ. Weights were assigned to these with $p = 0.04$. A decay correction of 15% over the 4 d of the experiment was applied, based on 400, 040, and 004 as standards. Absorption corrections ($\mu = 8.21$ mm^{-1}) calculated by analytical integration with the shape defined by six plane faces ranged from 1.705 to 2.223. The empirical correction factor for extinction was 1.12 for the strongest reflection, 100.

The density was measured by flotation in solutions of CHCl$_3$ and CCl$_4$. Various crystals which had been exposed to air for a long time had distinctly different densities, in the range 1.54 to 1.56 Mg m^{-3}. This variation, if due to differences in water content, would correspond to a loss of up to about 10% of the water from the nominal composition.

Crystal data

Co(C$_2$H$_8$N$_2$)$_3$(C$_4$H$_4$O$_6$)Cl.5H$_2$O, space group $P1$; at 298 K: $a = 8.261$ (3), $b = 8.507$ (3), $c = 8.149$ (3) Å, $\alpha = 101.20$ (1), $\beta = 95.27$ (1), $\gamma = 102.31$ (1)°, $Z = 1$, $V = 543.5$ Å^3, $D_x = 1.567$, $D_m = 1.54 - 1.56$ Mg m^{-3}.

Structure determination

The structure was solved using the Mo $K\alpha$ data. With only one Co atom in the unit cell it was possible to recognize the positions of the Cl and the C and N atoms of ethylenediamine from a three-dimensional Patterson function. An electron density difference function phased with that partial structure revealed the rest of the non-hydrogen atoms. The absolute configuration was adjusted to correspond to the known configuration of the (+)-tartrate ion. After least-squares refinement with anisotropic thermal parameters an electron density difference function revealed the positions of all of the H atoms. The final full-matrix refinement with isotropic thermal parameters for H and anisotropic for all other atoms (411 independent parameters) reduced $R_w = [\sum w(\Delta F)^2/\sum w|F_o|^2]^{1/2}$ to 0.024; the conventional $R = \sum|\Delta F|/\sum|F_o|$ was 0.022 for the 7688 reflections given weight, and 0.024 for all 7876 reflections. The resulting atomic coordinates are listed in Table 1.* The largest shift of any parameter in the last cycle was 7% of its standard deviation. The standard deviation of an observation of unit weight was 1.039.

The atomic scattering factors of Stewart, Davidson & Simpson (1965) were used for H and those of Doyle & Turner (1968) for the other atoms. The anomalous-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34240 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

scattering factors reported by Cromer & Liberman (1970) for Mo $K\alpha_1$ were used for Co, Cl, O, N, and C.

A refinement of the reverse configuration of the structure, which gave $R_w = 0.063$ and $R = 0.049$ for the 7688 reflections, confirms the absolute configuration and indicates how much effect $f'' = 0.973$ for Co has on the structure factors.

A less exhaustive refinement of the Cu $K\alpha$ data gave $R = 0.029$ and $R_w = 0.032$ for 3198 independent reflections ($I > 3\sigma$). The atomic coordinates are generally in good agreement with those in Table 1, but have standard deviations two or three times larger because of the lower resolution of the less extensive data set.

Description of the structure

Bond distances and bond angles are listed in Tables 2 and 3. The corresponding bromide salt is isomorphous and has a similar atomic arrangement according to Kushi, Kuramoto & Yoneda (1976), but numerical coordinates were not published. Pepinsky & Okaya (1956) also studied the bromide, but gave no details. The cation consists of a Co atom complexed to three ethylenediamine ligands in the form of a left-handed propeller as shown in Fig. 1. The absolute configuration, described as $\Lambda(+)_{589}[Co(en)_3\delta\delta\delta]^{3+}$ (IUPAC, 1970), has already been well established by several other studies by Saito, Nakatsu, Shiro & Kuroya (1955), Nakatsu (1962), Iwata, Nakatsu & Saito (1969), and Witiak, Clardy & Martin (1972). The dimensions of this complex have also been measured by Duesler & Raymond (1971), Veal & Hodgson (1972), Whuler, Brouty, Spinat & Herpin (1975), Brouty, Spinat, Whuler & Herpin (1976), and Haupt, Huber &
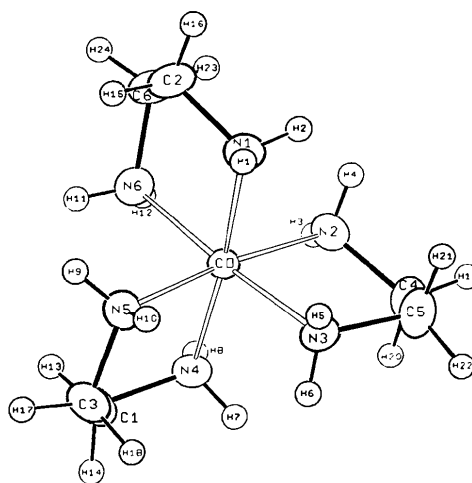

Fig. 1. The [Co(en)$_3$]$^{3+}$ ion.

Table 1. *Atom coordinates* ($\times 10^5$ *for* Cl; $\times 10^4$ *for* N, C, O; $\times 10^3$ *for* H) *for* (+)-[Co(C$_2$H$_8$N$_2$)$_3$]$^{3+}$.C$_4$H$_4$O$_6^{2-}$. Cl$^-$.5H$_2$O

E.s.d.'s of the least significant digits are given in parentheses.

	x	y	z		x	y	z
Co	0	0	0				
Cl	23162 (5)	−28567 (5)	−30803 (5)	H(6)	−9 (2)	−66 (2)	274 (3)
N(1)	324 (2)	2390 (2)	206 (2)	H(7)	−16 (2)	−274 (2)	54 (2)
N(2)	2409 (1)	133 (2)	93 (2)	H(8)	19 (2)	−274 (2)	−114 (3)
N(3)	396 (2)	274 (2)	2461 (2)	H(9)	−292 (2)	3 (2)	−73 (2)
N(4)	−446 (2)	−2411 (1)	−402 (2)	H(10)	−258 (2)	26 (3)	104 (3)
N(5)	−2418 (2)	−299 (2)	77 (2)	H(11)	−126 (2)	−48 (2)	−290 (2)
N(6)	−244 (2)	−143 (2)	−2452 (2)	H(12)	31 (2)	−83 (2)	−292 (2)
C(1)	−2260 (2)	−3121 (2)	−987 (2)	H(13)	−245 (3)	−309 (3)	−212 (3)
C(2)	−101 (2)	2744 (2)	−1468 (2)	H(14)	−252 (3)	−426 (3)	−78 (3)
C(3)	−3202 (2)	−2048 (2)	45 (2)	H(15)	−128 (3)	257 (2)	−173 (2)
C(4)	3032 (2)	−208 (2)	1719 (2)	H(16)	41 (3)	377 (3)	−149 (3)
C(5)	2221 (2)	696 (2)	3060 (2)	H(17)	−437 (2)	−229 (3)	−48 (2)
C(6)	422 (2)	1513 (2)	−2778 (2)	H(18)	−310 (2)	−220 (2)	126 (3)
C(7)	6874 (1)	2328 (1)	4322 (1)	H(19)	424 (3)	11 (3)	192 (3)
C(8)	7332 (1)	3736 (1)	3396 (1)	H(20)	269 (3)	−138 (3)	161 (3)
C(9)	9057 (1)	4796 (1)	4205 (1)	H(21)	267 (2)	186 (2)	321 (2)
C(10)	9584 (2)	6181 (1)	3272 (2)	H(22)	242 (3)	35 (3)	417 (3)
O(1)	6415 (2)	2720 (1)	5735 (1)	H(23)	165 (3)	164 (3)	−272 (3)
O(2)	7027 (1)	930 (1)	3641 (1)	H(24)	1 (3)	158 (3)	−386 (3)
O(3)	7350 (1)	3148 (1)	1644 (1)	H(25)	661 (2)	442 (2)	357 (2)
O(4)	10197 (1)	3760 (1)	4169 (1)	H(26)	896 (2)	527 (2)	531 (2)
O(5)	8840 (2)	7328 (1)	3520 (2)	H(27)	650 (3)	322 (3)	118 (3)
O(6)	10654 (1)	6090 (1)	2299 (1)	H(28)	1097 (3)	421 (3)	463 (3)
O(7)	4310 (1)	3632 (1)	387 (2)	H(29)	443 (4)	398 (4)	−46 (4)
O(8)	6460 (2)	8262 (2)	5158 (2)	H(30)	415 (3)	439 (3)	99 (3)
O(9)	4078 (2)	4210 (2)	7204 (2)	H(31)	639 (3)	901 (3)	465 (3)
O(10)	5205 (2)	624 (2)	7741 (2)	H(32)	696 (3)	790 (3)	473 (3)
O(11)	3816 (2)	5711 (3)	3086 (2)	H(33)	473 (4)	402 (3)	666 (4)
H(1)	−22 (3)	284 (3)	91 (3)	H(34)	381 (3)	492 (4)	698 (4)
H(2)	136 (3)	283 (2)	51 (2)	H(35)	539 (4)	111 (4)	705 (4)
H(3)	263 (2)	−57 (2)	−70 (3)	H(36)	475 (4)	−32 (4)	713 (4)
H(4)	298 (2)	110 (2)	−1 (2)	H(37)	293 (4)	574 (4)	296 (3)
H(5)	−1 (3)	111 (3)	296 (3)	H(38)	443 (4)	663 (4)	365 (5)

Table 2. *Distances* (Å)

Tris(ethylenediamine)cobalt(III)

Co−N(1)	1·965 (1)	N(5)−C(3)	1·484 (2)	N(3)−H(6)	0·89 (2)	C(2)−H(16)	0·89 (2)
Co−N(2)	1·962 (1)	N(6)−C(6)	1·484 (2)	N(4)−H(7)	0·90 (2)	C(3)−H(17)	0·98 (2)
Co−N(3)	1·962 (1)	C(1)−C(3)	1·507 (2)	N(4)−H(8)	0·88 (2)	C(3)−H(18)	1·03 (2)
Co−N(4)	1·961 (1)	C(2)−C(6)	1·505 (2)	N(5)−H(9)	0·87 (2)	C(4)−H(19)	0·96 (2)
Co−N(5)	1·968 (1)	C(4)−C(5)	1·504 (2)	N(5)−H(10)	0·87 (2)	C(4)−H(20)	0·96 (2)
Co−N(6)	1·967 (1)	N(1)−H(1)	0·85 (2)	N(6)−H(11)	0·85 (2)	C(5)−H(21)	0·96 (2)
N(1)−C(2)	1·481 (2)	N(1)−H(2)	0·85 (2)	N(6)−H(12)	0·87 (2)	C(5)−H(22)	1·02 (2)
N(2)−C(4)	1·480 (2)	N(2)−H(3)	0·85 (2)	C(1)−H(13)	0·93 (2)	C(6)−H(23)	1·00 (2)
N(3)−C(5)	1·485 (2)	N(2)−H(4)	0·88 (2)	C(1)−H(14)	1·00 (2)	C(6)−H(24)	0·93 (2)
N(4)−C(1)	1·486 (2)	N(3)−H(5)	0·90 (2)	C(2)−H(15)	0·95 (2)		

Tartrate

C(7)−O(1)	1·251 (2)	C(7)−C(8)	1·536 (2)	C(8)−O(3)	1·421 (1)	C(8)−H(25)	0·92 (2)
C(7)−O(2)	1·249 (2)	C(8)−C(9)	1·525 (2)	C(9)−O(4)	1·419 (1)	C(9)−H(26)	0·93 (2)
C(10)−O(5)	1·254 (2)	C(9)−C(10)	1·531 (2)			O(3)−H(27)	0·78 (2)
C(10)−O(6)	1·246 (2)					O(4)−H(28)	0·70 (3)

Water

O(7)−H(29)	0·81 (3)	O(8)−H(32)	0·65 (3)	O(9)−H(34)	0·74 (3)	O(10)−H(36)	0·85 (3)
O(7)−H(30)	0·77 (3)	O(9)−H(33)	0·75 (3)	O(10)−H(35)	0·77 (3)	O(11)−H(37)	0·74 (3)
O(8)−H(31)	0·83 (3)					O(12)−H(38)	0·85 (3)

Table 3. *Angles* (°)

Tris(ethylenediamine)cobalt(III)

N(1)–Co–N(2)	92·4 (1)	N(3)–Co–N(6)	175·7 (1)	H(3)–N(2)–H(4)	105 (2)
N(1)–Co–N(3)	91·6 (1)	N(4)–Co–N(5)	85·6 (1)	H(5)–N(3)–H(6)	110 (3)
N(1)–Co–N(4)	174·9 (1)	N(4)–Co–N(6)	89·9 (1)	H(7)–N(4)–H(8)	107 (2)
N(1)–Co–N(5)	92·2 (1)	N(5)–Co–N(6)	93·2 (1)	H(9)–N(5)–H(10)	108 (2)
N(1)–Co–N(6)	85·5 (1)	Co–N(1)–C(2)	110·0 (1)	H(11)–N(6)–H(12)	108 (2)
N(2)–Co–N(3)	85·4 (1)	Co–N(2)–C(4)	108·7 (1)	H(13)–C(1)–H(14)	114 (3)
N(2)–Co–N(4)	90·2 (1)	Co–N(3)–C(5)	110·1 (1)	H(15)–C(2)–H(16)	111 (3)
N(2)–Co–N(5)	173·7 (1)	Co–N(4)–C(1)	109·1 (1)	H(17)–C(3)–H(18)	112 (2)
N(2)–Co–N(6)	91·5 (1)	Co–N(5)–C(3)	110·4 (1)	H(19)–C(4)–H(20)	108 (3)
N(3)–Co–N(4)	93·0 (1)	Co–N(6)–C(6)	109·2 (1)	H(21)–C(5)–H(22)	110 (2)
N(3)–Co–N(5)	90·1 (1)	H(1)–N(1)–H(2)	109 (3)	H(23)–C(6)–H(24)	108 (3)

Tartrate

O(1)–C(7)–O(2)	126·1 (1)	C(8)–C(9)–O(4)	108·3 (1)	C(9)–C(8)–H(25)	106 (1)
O(1)–C(7)–C(8)	115·5 (1)	O(4)–C(9)–C(10)	112·1 (1)	C(8)–O(3)–H(27)	107 (2)
O(2)–C(7)–C(8)	118·4 (1)	C(9)–C(10)–O(5)	115·9 (1)	C(8)–C(9)–H(26)	107 (1)
C(7)–C(8)–O(3)	112·4 (1)	C(9)–C(10)–C(6)	119·6 (1)	O(4)–C(9)–H(26)	111 (1)
C(7)–C(8)–C(9)	108·4 (1)	O(5)–C(10)–O(6)	124·3 (1)	C(10)–C(9)–H(26)	108 (1)
O(3)–C(8)–C(9)	109·5 (1)	C(7)–C(8)–H(25)	110 (1)	C(9)–O(4)–H(28)	109 (2)
		O(3)–C(8)–H(25)	111 (1)		

Water

H(29)–O(7)–H(30)	101 (4)	H(33)–O(9)–H(34)	107 (4)	H(37)–O(11)–H(38)	112 (4)
H(31)–O(8)–H(32)	101 (4)	H(35)–O(10)–H(36)	100 (4)		

Preut (1976). Our bond distances fell within the ranges listed in most of the earlier reports. Our confidence in their accuracy is enhanced by the high degree of consistency of values for bonds which are chemically equivalent.

Chemically equivalent bonds in the tartrate ion also have closely similar lengths, and are in good agreement generally with other studies of tartrate and bitartrate salts (van Bommel & Bijvoet, 1958; Ambady & Kartha, 1968; Hinazumi & Mitsui, 1972; Yadava & Padmanabhan, 1973; Pérez, 1976, 1977; Templeton & Templeton, 1978). The molecular conformation and atomic numbering scheme are shown in Fig. 2. The

absolute configuration is the same as that first demonstrated for (+)-tartrate by Bijvoet, Peerdeman & van Bommel (1951).*

The chloride ion is near one cobalt complex on the pseudo threefold axis of the octahedron (Fig. 3). Its six nearest neighbors are H atoms (attached to N or O) at distances from 2·42 to 2·75 Å. The corresponding Cl–O and Cl–N distances range from 3·18 to 3·32 Å and 3·24 to 3·45 Å, respectively (Table 4), and have geometries appropriate for weak hydrogen bonds. All the other H atoms on N or O are located near lines to O neighbors at N–O distances 2·89 to 3·22 Å or O–O distances 2·65 to 2·86 Å (Table 4). In each case the bond angles are appropriate for hydrogen bonding, but the bonding must be rather weak in the case of the longer N–O distances.

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* While (+)-tartrate is commonly designated as D-tartrate in the earlier literature, it may be noted that the current practice in carbohydrate chemistry (IUPAC, 1972) is to use L to describe this absolute configuration.
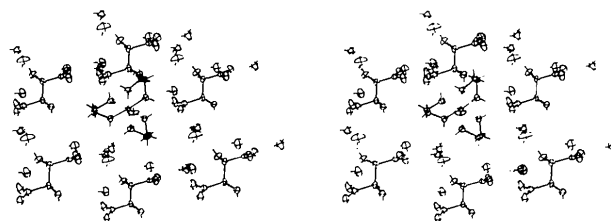

Fig. 2. The (+)-tartrate ion, $C_4H_4O_6^{2-}$.

Fig. 3. Packing diagram as viewed down the pseudo threefold axis of the cation.

Table 4. *Hydrogen-bond distances and angles*

Standard deviations are 0·002 Å for each distance and 0·1° for each angle.

O(3)—N(1)—O(7)	2·956 Å	3·216 Å	144·2°
Cl—N(2)—O(7)	3·239	3·007	123·8
O(4)—N(3)—O(5)	3·066	2·889	123·9
Cl—N(4)—O(6)	3·328	2·918	103·2
O(2)—N(5)—O(10)	3·001	2·941	109·2
Cl—N(6)—O(8)	3·448	3·078	107·1
O(9)—O(7)—O(11)	2·729	2·663	123·6
O(2)—O(8)—O(5)	2·765	2·649	85·5
Cl—O(9)—O(1)	3·180	2·765	139·8
Cl—O(10)—O(1)	3·292	2·743	132·0
O(6)—O(11)—O(8)	2·733	2·865	123·6
O(7)—O(3)	2·768		
Cl—O(4)	3·316		

Anomalous scattering

Anomalous-scattering effects are not especially large for this crystal and Mo $K\alpha$ radiation, but they are significant. We used the Mo radiation data set to determine f'' for both Co and Cl by the method of least squares (Templeton & Templeton, 1978). Both can be determined because they contribute differently to different reflections. Not *all* the f'' values can be determined, because it is necessary to have a definition of zero phase angle. In the present example, the considerable number of O, N, C and H atoms give that definition. We assume for them that the rather small values of f'' calculated by Cromer & Liberman (1970) are correct. In principle one could also determine f'' for some of the light atoms, using just one element as a standard, but there are other substances which seem more suitable for that objective.

A refinement with only a scale factor and f'' for Co and Cl as variables, using the values determined above for all the other parameters, yielded the values listed in Table 5, which are in excellent agreement with those calculated by Cromer & Liberman (1970) for Mo $K\alpha_1$. Another calculation, refining f'' of Co, a scale factor, and all positional and thermal parameters of Co, Cl and six N atoms (except xyz of Co) yielded $f'' = 0·964 \pm 0·009$ and trivial changes of other parameters; this

Table 5. *Anomalous-scattering terms*

	λ (Å)	Experiment	Theory[a]
f''(Co)	0·711[b]	0·962 (10)	0·973
	1·542[c]	3·92 (2)	3·608
f'(Co)	1·542	−2·36 (2)	−2·464
f''(Cl)	0·711	0·155 (10)	0·159
	1·542	0·72 (2)	0·702
f'(Cl)	1·542	0·23 (2)	0·348

Notes: (a) Cromer & Liberman (1970) at $K\alpha_1$, (b) Mo $K\bar{\alpha}$, (c) Cu $K\bar{\alpha}$.

calculation confirms that f'' is not much correlated with other parameters. As a test of the variation of f'' with scattering angle, a calculation with f'' defined as a linear function of $s^2 = (\sin^2\theta)\lambda^{-2}$ yielded:

$$f''(\text{Co}) = (0·97 \pm 0·02) - (0·02 \pm 0·08)s^2, \text{Mo } K\alpha$$

$$f''(\text{Cl}) = (0·15 \pm 0·02) + (0·01 \pm 0·08)s^2.$$

In this case the thermal parameters of Co and Cl were allowed to vary, but they hardly changed. These results show no change with angle at the accuracy of the experiment; we report them to set an upper limit on the effect.

It is evident in advance that f' will be more sensitive than f'' to changes in scale factor or thermal parameters or to any errors in the experiment or thermal model which are correlated with diffraction angle. However, as an experiment we made a calculation with scale factor and f', f'', and thermal parameters for Co and Cl as variables. The results were $f'(\text{Co}) = 0·20$ (2) and $f'(\text{Cl}) = 0·06$ (2), surprisingly close to the values 0·299 and 0·132 calculated by Cromer & Liberman (1970); the estimated standard deviations, however, appear to be unrealistic, and we expect that systematic errors are present. The values obtained for f'', 0·957 (10) for Co and 0·156 (10) for Cl, are nearly the same as before. Correlation coefficients between each f' and the diagonal anisotropic thermal parameters of the same atom ranged from 0·66 to 0·74.

In all of the above calculations the R values were almost identical, as is to be expected in view of the small changes in the scattering factors which resulted.

The Cu data set was refined with a scale factor and anomalous-scattering terms for Co and Cl as variables. All coordinates and thermal parameters were held at the values determined with the Mo $K\alpha$ data set. Anomalous-scattering terms for C, O, and N were taken from Cromer & Liberman (1970). The results in Table 5 were obtained with $R = 0·029$ and $R_w = 0·035$. This value of R_w is not quite as good as that obtained in the earlier refinement, but one must note that it is achieved with only five adjustable parameters rather than 411. There is a significant discrepancy with the value calculated by Cromer & Liberman (1970) for f'' of Co; pending further investigation we ascribe it to the effect called extended X-ray absorption fine structure (EXAFS) which is expected to occur at this photon energy which is only about 300 eV from the Co K edge. The theoretical value is calculated for an isolated atom which is free of this effect.

A calculation to test the variation of f'' with angle for Co and Cl yielded the values

$$f''(\text{Co}) = (4·01 \pm 0·04) - (0·6 \pm 0·2)s^2, \text{Cu } K\alpha$$

$$f''(\text{Cl}) = (0·69 \pm 0·04) + (0·2 \pm 0·3)s^2,$$

where $s = \lambda^{-1}\sin\theta$ as before. In this refinement also R

$= 0.029$ and $R_w = 0.035$. The variation of $f''(\text{Cl})$ with angle is not significant. The equation for $f''(\text{Co})$ gives $f'' = 3.8$ at $\theta = 63°$, the upper limit of the experiment. This 5% reduction (relative to zero angle) is similar to the 3·3% reduction at this angle estimated by Hazell (1975) from orbital Fourier transforms, an approximate method which may be expected to give the order of magnitude of the change. Thus our result is plausible, but it must be regarded as tentative because of the marginal statistical significance and because some calculations with the data partitioned into shells for intervals of s indicate some small systematic errors of unidentified origin which are correlated with diffraction angle. However, our result serves to define an upper limit for this effect which still lacks any definitive measurement. Hall & Maslen (1966) report a somewhat similar result for f'' of iodine at Cu $K\alpha$.

The decay of intensity indicated by the repetitive measurements of the standard reflections is one possible source of error in these results. It is not expected to have a first-order effect on the calculated scattering terms because the effects of form factors in structure factors have little to do with the sequence of the measurements. To the extent that the decay correction does not remove the errors, the effects should be reflected in the estimated standard deviations obtained in the least-squares procedure.

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