

This feature is also present in the calculated bond distances for pyrazole (Dewar & Gleicher, 1966).

The planarity of the pyrazole rings and the narrow range of bond distances indicate that resonance is important in the description of the pyrazole molecule. The proximity of the nickel ion may be expected to reduce the electron density in the rings which would decrease the resonance and act to restore the single and double bond distances toward their classical values. If this is the case, a variable coordinate bond distance may be accompanied by measurable changes in the ring bond distances. In the structure of the three pyrazole complexes, the distances from the nickel ion to the coordinated nitrogen atom have five different values from 2.080 to 2.125 Å. A sensitive indicator of a change in resonance would be the difference (Δ) be-

tween the longest [C(1)–C(2)] and shortest [N(1)–C(1)] bond lengths. In Table 6 this difference (Δ) is given along with the corresponding Ni···N coordinate distance. The values in the Table show that although the differences are small there is a trend in the expected direction; *i.e.* Δ decreases with increasing coordination distance. It should be pointed out that the calculated bond distances for non-coordinated pyrazole (Dewar & Gleicher, 1966) have a $\Delta=0.16$ which is greater than that observed in any of the five coordinated pyrazole molecules discussed here. This suggests that the resonance contribution to the structure of non-coordinated pyrazole may have been underestimated in the theoretical calculations.

All computer calculations on this structure were performed using the *Program System for X-ray Crystallography* (1967) developed at the University of Maryland in collaboration with the National Bureau of Standards and the Geological Survey. The authors would like to thank Floyd Mauer of NBS and Professor P. Willis of Hood College for their assistance in the collection and processing of the diffraction data.

Table 6. Correlation between the Ni···N coordinate bond distance and (Δ) in three pyrazole complexes

Δ is defined as the difference between the shortest ring bond distance [N(1)–C(1)] and the longest ring bond distance [C(1)–C(2)].

Coordinate bond distance

[Ni···N]	$\Delta = \{[C(1)-C(2)] - [N(1)-C(1)]\}$
2.125 Å*	0.049 Å
2.101 †	0.057
2.097 ‡	0.064
2.087 †	0.068
2.080 †	0.078

* Hexapyrazolenickel(II) nitrate, Ni(Pz)₆(NO₃)₂ (this paper). In this compound there is one crystallographically independent pyrazole ring.

† Dibromotetrapyrazolenickel(II), Ni(Pz)₄Br₂. (Mighell *et al.*, 1969). In this compound there are two crystallographically independent pyrazole rings.

‡ Dichlorotetrapyrazolenickel(II), Ni(Pz)₄Cl₂. (Reimann *et al.*, 1967). In this compound there are two crystallographically independent pyrazole rings.

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The Crystal Structure of the 1:4 Calcium Bromide–Diacetamide Complex

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The crystal structure of CaBr₂·4C₄H₇NO₂ has been determined by three-dimensional X-ray methods. Data were collected by automatic counting methods and agreement of $R=0.08$ was obtained after full-matrix anisotropic refinement. Each calcium ion was found to be chelated by four molecules of diacetamide and to lie at the centre of an antiprism defined by the eight oxygen ligands. The bromide ions do not occur in the calcium coordination spheres, but lie halfway between nitrogen atoms within layers of diacetamide molecules parallel to (001).

Introduction

According to the mechanism proposed for the complexing of alkali metal halides with diacetamide (Roux

& Boeyens, 1969*b*) one would expect alkaline earth metal halides to form 1:2 complexes in which the metal ion lies centrally in the plane of four oxygen ligands and with two halide ions completing a coordination octahedron around it. These salts, however, invariably form 1:4 complexes (Gentile & Shankoff, 1965) and their geometries can thus be expected to be of a differ-

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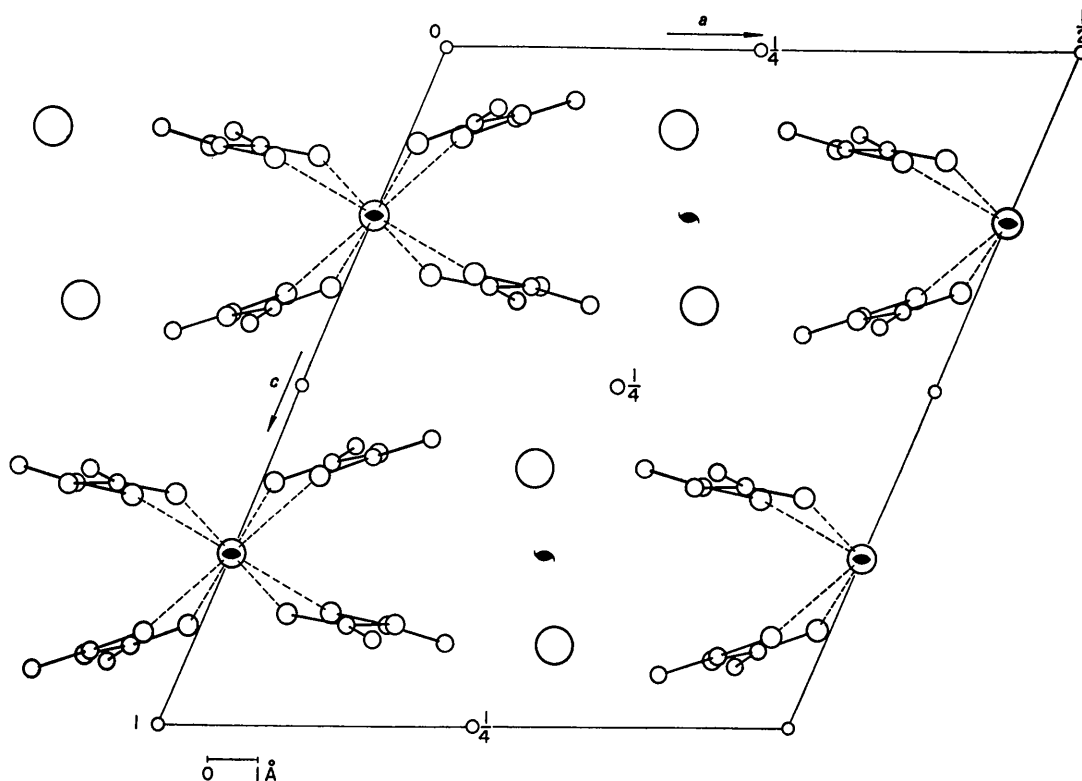


Fig. 1. Projection of the structure along [010]. The calcium ions lie on twofold axes and are bonded to the oxygen atoms of diacetamide molecules. The isolated circles represent bromide ions.

ent type. To establish this arrangement, the structure of $\text{CaBr}_2 \cdot 4(\text{CH}_3\text{CO} \cdot \text{N} \cdot \text{COCH}_3)$ was determined and is reported in this paper.

Experimental

The complex was prepared according to the method of Gentile & Shankoff (1965) and recrystallized from absolute methanol. A cube-like crystal ($0.44 \times 0.36 \times 0.4 \text{ mm}^3$) was cut from a well developed large cylindrical crystal and sealed into a Lindemann capillary to prevent the slow decomposition which occurs on exposure to the atmosphere. Preliminary cell dimensions were obtained from oscillation, Weissenberg and precession photographs. The values as refined on a Hilger & Watts four-circle diffractometer are:

$$\begin{aligned} a &= 24.91 \pm 0.02 \text{ \AA} \\ b &= 8.089 \pm 0.006 \\ c &= 14.33 \pm 0.015 \\ \beta &= 113.35 \pm 0.01^\circ \end{aligned}$$

The reflexion conditions of hkl : $h+k=2n$, $h0l$: $l=2n$ are consistent with the space groups Cc and $C2/c$. The successful structure analysis confirmed the latter centrosymmetric space group (No. 15 in *International*

Tables for X-ray Crystallography, 1965). The density was measured as 1.48 g.cm^{-3} and calculated as 1.51 g.cm^{-3} for $Z=4$.

The intensities of all reflexions within the copper sphere were measured diffractometrically with an ω -scan and $\text{Mo K}\alpha$ (Zr filter) radiation. More reliable background statistics are obtained with the ω -scan, but it has the disadvantage that white radiation contributions from nearby reflexions on the same central lattice row are included in the integrated intensity. A computer program was written to correct for this effect in terms of a general reflexion profile obtained by scanning an isolated and relatively strong reflexion in θ . After L_p correction this profile was normalized as a function of $(\sin \theta)/\lambda$ so that its interference at the position of any neighbouring reflexion could be computed directly. Finally a composite scattering curve for $\text{CaBr}_2 \cdot 4(\text{diacetamide})$ was constructed to adjust the correction term according to the values of $(\sin \theta)/\lambda$ at which mutual interferences occur. This correction, which appears to be similar to that described by Hoppe (1969), was applied only in the final stages of refinement and was found to lead to an improvement of only 0.1% in R .

Observations at the positions of the systematically absent reflexions established a minimum meaningful

STRUCTURE OF THE 1:4 CALCIUM BROMIDE-DIACETAMIDE COMPLEX

Table 1. Observed and calculated structure factors on an absolute scale

Table with 16 columns of structure factor data (h, k, l, F_o, F_c) and rows corresponding to various Miller indices (hkl) such as h00, 100, 110, etc., up to 111 31 28.

count of 35. Of the total of 2861, the 988 reflexions counted as 35 or less above the background were treated as unobserved. As suggested by Dunning & Vand (1969), they were left out in the final refinement if calculated below the limiting value. No correction was applied for absorption ($\mu R \text{ Mo } K\alpha = 0.9$), but all the other usual corrections were applied as described before (Roux & Boeyens, 1969a).

Determination and refinement of the structure

The coordinates of the bromide and calcium ions were determined from the Harker sections of a three-dimensional Patterson synthesis and used to phase a three-dimensional Fourier synthesis from which the positions of the carbon, nitrogen and oxygen atoms were obtained. A three-dimensional difference synthesis which was calculated next showed the trial structure to be essentially correct and revealed severe anisotropy.

The trial structure was refined using a full-matrix least-squares program which minimizes the quantity $\sum w(F_o - |kF_c|)^2$. No differential weighting was applied. The refinement was considered complete when all parameter shifts were less than 0.1 of the estimated standard deviations. At this stage the discrepancy, defined as $R = \sum |AF| / \sum F_o$, was 0.078. The observed and

final calculated structure factors on an absolute scale ($F(000) = 306$) are listed in Table 1 and the final coordinates in Table 2. The corresponding interatomic distances and angles are given in Table 3. The atomic scattering factors and computer programs used in this analysis have been cited before (Roux & Boeyens, 1969a).

Description of the structure

The clearest view of the structure is provided by the (010) projection shown in Fig. 1. The calcium ions on the set of $0, y, \frac{1}{2}$ twofold axes at $y = 0.093$ are seen to be chelated through the oxygen atoms of four diacetamide molecules with an average Ca-O distance of 2.42 Å. The spatial arrangement of these ($\text{Ca}^{2+} \cdot 4\text{diacetamide}$) coordination units is better illustrated by the projection along [100] shown in Fig. 2. They are seen to occur in stacks along [001]. The geometry of a coordination sphere is antiprismatic as shown in Fig. 3. Apart from bridging through bromide ions the only interaction among these coordination units is of the van der Waals type.

As seen from Fig. 1 and 2, the coordination units are bridged by bromide ions into layers parallel to (001). Each bromide ion lies between the nitrogen atoms associated with diacetamide molecules in neighbouring

Table 2. Fractional coordinates and anisotropic thermal parameters, where $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$

Standard deviations are given below each value.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.21125	0.19119	0.11904	0.00203	0.04064	0.01021	-0.00448	0.00253	0.00059
	0.00006	0.00024	0.00011	0.00003	0.00046	0.00011	0.00009	0.00005	0.00018
Ca	0.0	0.92782	0.25000	0.00100	0.00994	0.00461	0.0	0.00114	0.0
		0.00035		0.00005	0.00046	0.00017		0.00007	
O(1)	0.00836	0.14539	0.14193	0.00161	0.01705	0.00854	0.00067	0.00217	0.00292
	0.00027	0.00094	0.00055	0.00014	0.00145	0.00057	0.00037	0.00024	0.00075
O(1')	0.04287	0.82763	0.13253	0.00215	0.01283	0.00782	-0.00100	0.00297	-0.00205
	0.00029	0.00086	0.00053	0.00015	0.00126	0.00052	0.00037	0.00025	0.00067
O(2)	0.09893	0.03173	0.33484	0.00113	0.01455	0.00742	0.00094	0.00111	-0.00122
	0.00025	0.00084	0.00053	0.00013	0.00133	0.00051	0.00033	0.00021	0.00067
O(2')	0.06502	0.71265	0.33834	0.00167	0.01907	0.00989	0.00139	0.00228	0.00284
	0.00029	0.00099	0.00058	0.00015	0.00159	0.00063	0.00042	0.00026	0.00084
N(1)	0.08355	0.06060	0.09874	0.00158	0.01589	0.00691	-0.00086	0.00202	0.00012
	0.00034	0.00115	0.00064	0.00016	0.00168	0.00062	0.00046	0.00027	0.00035
N(2)	0.15573	0.79970	0.35332	0.00160	0.01310	0.00777	0.00032	0.00172	-0.00084
	0.00034	0.00113	0.00066	0.00017	0.00164	0.00065	0.00045	0.00028	0.00089
C(1)	0.04780	0.18094	0.11328	0.00152	0.01564	0.00629	-0.00166	0.00129	-0.00065
	0.00041	0.00137	0.00077	0.00019	0.00205	0.00071	0.00056	0.00031	0.00108
C(1')	0.07863	0.89116	0.10504	0.00160	0.01183	0.00450	-0.00014	0.00147	0.00008
	0.00040	0.00120	0.00069	0.00020	0.00186	0.00060	0.00046	0.00029	0.00078
C(2)	0.14782	0.96941	0.35559	0.00141	0.01676	0.00450	0.00126	0.00073	-0.00084
	0.00040	0.00135	0.00072	0.00019	0.00227	0.00062	0.00051	0.00027	0.00091
C(2')	0.11576	0.67984	0.35358	0.00205	0.02028	0.00563	0.00174	0.00138	0.00016
	0.00046	0.00156	0.00079	0.00024	0.00247	0.00071	0.00067	0.00034	0.00115
Me(1)	0.06007	0.35362	0.09076	0.00309	0.01163	0.01116	-0.00077	0.00303	0.00192
	0.00055	0.00148	0.00103	0.00032	0.00210	0.00111	0.00065	0.00050	0.00122
Me(1')	0.12140	0.79200	0.07777	0.00236	0.02150	0.00939	0.00100	0.00345	-0.00091
	0.00047	0.00160	0.00089	0.00025	0.00254	0.00090	0.00069	0.00042	0.00130
Me(2)	0.20128	0.07218	0.38073	0.00101	0.02126	0.01008	-0.00062	0.00142	-0.00214
	0.00040	0.00158	0.00091	0.00018	0.00243	0.00097	0.00059	0.00035	0.00131
Me(2')	0.14150	0.50764	0.37766	0.00283	0.01310	0.01350	0.00185	0.00298	0.00079
	0.00058	0.00152	0.00114	0.00032	0.00208	0.00127	0.00069	0.00054	0.00142

Table 3. *Interatomic distances and angles with standard deviations*

Bond	Distance (Å)	Angle	Angle (°)
N(1)-Br	3.253 ± 0.007	O(1)*-Ca-O(1')*	68.2 ± 0.24
N(2)-Be	3.296 ± 0.008	O(1')*-Ca-O(2')	77.5 ± 0.23
O(1)-Ca	2.408 ± 0.007	O(2')-Ca-O(2)	69.1 ± 0.25
O(1')-Ca	2.461 ± 0.006	O(2)-Ca-O(1)*	75.7 ± 0.22
O(2)-Ca	2.425 ± 0.006	O(1')*-O(2')-O(2)	90.6 ± 0.28
O(2')-Ca	2.373 ± 0.007	O(2')-O(2)-O(1)*	89.5 ± 0.26
C(1)-N(1)	1.389 ± 0.013	O(2)-O(1')*-O(1')*	91.7 ± 0.27
C(1')-N(1)	1.382 ± 0.013	O(1')*-O(1')*-O(2')	88.2 ± 0.26
C(2)-N(2)	1.389 ± 0.014	O(1')*-O(2')*-O(2')*	59.4 ± 0.24
C(2')-N(2)	1.391 ± 0.014	O(2')*-O(2')*-O(1')*	67.4 ± 0.26
C(1)-O(1)	1.239 ± 0.011	O(2')*-O(1')*-O(2')*	53.1 ± 0.24
C(1')-O(1')	1.221 ± 0.010	O(2)-O(1')-O(1)	59.6 ± 0.23
C(2)-O(2)	1.240 ± 0.010	O(1')-O(1)-O(2)	67.2 ± 0.25
C(2')-O(2')	1.223 ± 0.011	O(1)-O(2)-O(1')	53.2 ± 0.23
C(1)-Me(1)	1.492 ± 0.015	O(2')-O(2')*-O(1')	55.8 ± 0.23
C(1')-Me(1')	1.504 ± 0.013	O(2')*-O(1')-O(2')	65.6 ± 0.28
C(2)-Me(2)	1.488 ± 0.014	O(1')-O(2)-O(2')*	58.6 ± 0.26
C(2')-Me(2')	1.515 ± 0.016	O(1)*-O(1)-O(2)*	55.8 ± 0.22
O(1)-O(2)	2.939 ± 0.010	O(1)-O(2)*-O(1)*	67.6 ± 0.27
O(2)-O(1')	3.143 ± 0.01	O(2)*-O(1')*-O(1)	56.6 ± 0.24
O(1)-O(1')	2.730 ± 0.01		
O(1')-O(2')	2.930 ± 0.01		
O(1')-O(2')*	3.025 ± 0.009		
O(2')-O(2')*	3.225 ± 0.014		
O(2')-C(2)	2.722 ± 0.011		
O(2)-O(1)*	2.967 ± 0.009		
O(1)-O(1)*	3.286 ± 0.014		

* Related by a twofold axis to the equivalent unstarred atom.

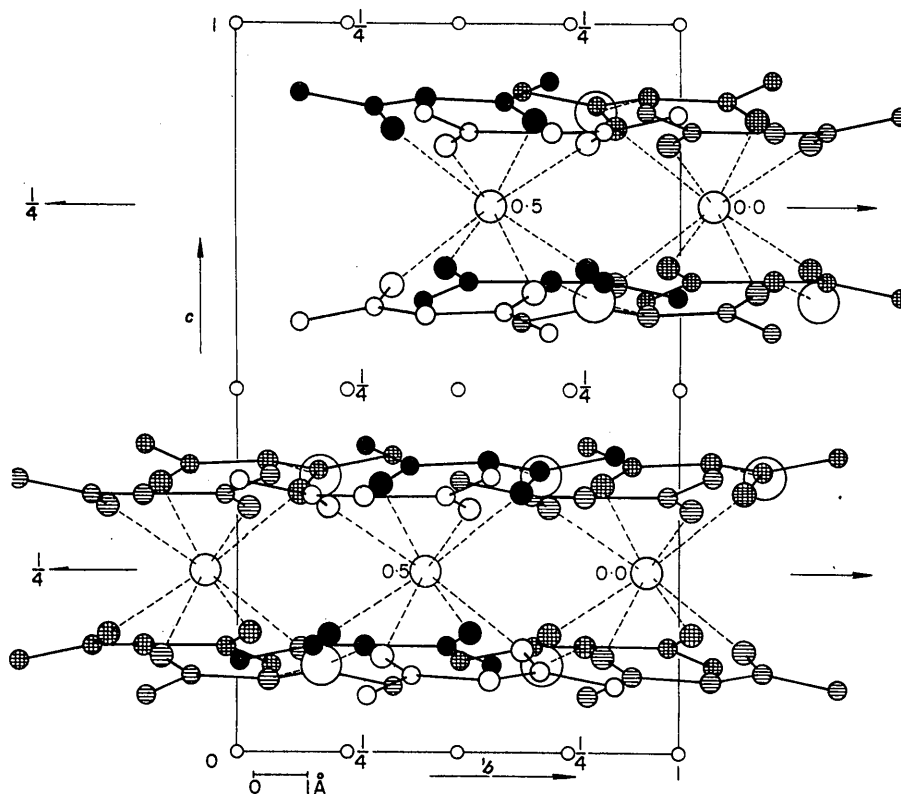


Fig. 2. Projection of the structure along [100]. Diacetamide molecules represented by connected open or black circles are chelated to cations with fractional x coordinates of $ca. 0.5$. Those represented by hatched circles surround cations with $x \sim 0$.

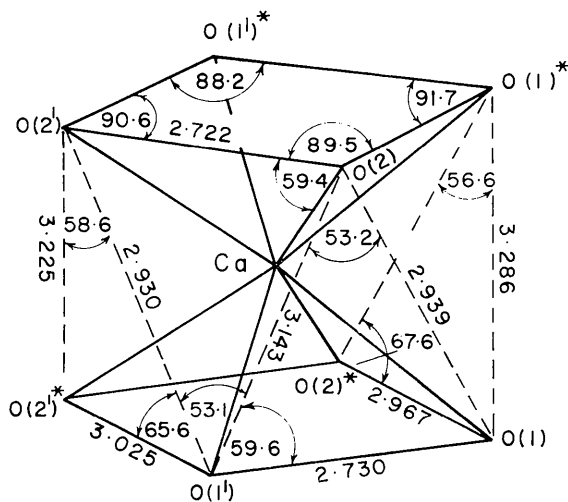


Fig. 3. Perspective view of a (Ca-O₈) coordination unit. Unstarred labels with the same indices (one primed) refer to oxygen atoms belonging to a single diacetamide molecule. An asterisk indicates an oxygen atom related by the two-fold axis to the oxygen atom with the same index.

coordination units. The average Br-N separation is 3.28 Å. The N-Br-N angle is 176°.

Discussion

This structure differs from the structures of the diacetamide complexes of the alkali halides (Roux & Boey-

ens, 1969a,b) in that there is no nearest-neighbour interaction between cation and anion. In this respect it corresponds with the ionic thiourea complexes (Boeyens & Herbstein, 1967) where complete segregation of anions and cations occurs. Unlike the alkali halide complexes of diacetamide, but like the thiourea complexes (Boeyens & Gafner, 1968), the CaBr₂·4(diace-tamide) thus appears to be a simple ion-dipole complex. Whether or not the NH-Br contact of 3.28 Å should be interpreted as a hydrogen bond as suggested by the infrared study of Gentile & Shankoff (1965), is not clear.

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The Squared-Tangent Formula*

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In the noncentrosymmetric space groups, the values of the squares of the tangents of a basic set of phases determine the values of the squares of the tangents of others, provided that the crystal structure consists of identical atoms. In selected, noncentrosymmetric space groups, *e.g.* $P2_12_12_1$, the square of the tangent of any phase is uniquely determined by the magnitudes alone of the structure factors. Hence, in the latter space groups, it is expected that the formulas derived here will supplement the older tangent formula and will facilitate the early determination of the values of certain phases.

1. Introduction

It has long been known that, for structures consisting of N identical atoms in the unit cell, a number of relationships among the structure factors exist. One of

these is the so-called tangent formula (Karle & Hauptman, 1956),

$$\tan \varphi_{\mathbf{h}} = \frac{\langle |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \sin (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}}}{\langle |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \cos (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}) \rangle_{\mathbf{k}}}, \quad (1.1)$$

in which φ denotes the phase of the normalized structure factor E , the vector \mathbf{h} is fixed, and the averages are extended over the same set of vectors \mathbf{k} . Equation (1.1)

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