$$a_{ij} = -J_{ij}J_{ji} = a_{ji} \quad \text{and:} \quad a_{ii} = \sum_{k=1}^{n} J_{ik}^2 \, .$$

Then equations (4) reduce to:

$$\sum_{j=1}^{n} a_{ij}k_j = 0, \quad i = 1 \text{ to } n \, .$$

As these n equations in n unknowns are not linearly independent, one can arbitrarily specify the value of one variable and reject one equation as redundant. Let us define $x_j = k_j/k_n$ and reject the nth equation. Then the new set of $n-1$ independent equations is:

$$\sum_{j=1}^{n-1} a_{ij}x_j = -a_{in}, \quad i = 1 \text{ to } n-1 \, . \tag{5}$$

These equations may be solved by various standard methods; for our work this is done with an existing Edsac II computer subroutine.

If it is inconvenient to solve the simultaneous equations directly and if trial values of the scaling constants are known, then the constants can be quickly refined using a variant of equation (4):

$$k_i = \frac{\sum_{j=1}^{n} k_j' J_{ij} J_{ji}}{\sum_{j=1}^{n} J_{ij}^2} \tag{6}$$

where the primed k's are the trial values and the new values are 'normalized' after each cycle by dividing through by some k_n.

It is of interest to compare the functions minimized in the two methods. Kraut uses as the ratio between two planes the average value of the ratios between individual reflections, thus emphasizing the contributions of weak reflections. We use the ratio of the sums of all corresponding reflections on the two films, emphasizing the strong reflections. (This can be compensated for by some weighting method such as rejecting the strongest intensities for scaling or using scattering amplitudes instead of intensities, thus producing an effective weighting factor of $I^{-\frac{1}{2}}$.) If only medium intensities are used the two types of ratio will be quite similar in value. If one uses the latter ratio in Kraut's equations (1) and (2) above, then:

$$r_{ij} = J_{ji}/J_{ij} = (r_{ji})^{-1}$$

$$k_i = \prod_{j=1}^{n} (r_{ij}/r_{nj})^{1/n} \tag{1'}$$

and the quantity minimized is:

$$F(k_i, J_{ij}) = \sum_{i=1}^{n}\sum_{j=1}^{n} (\log k_i J_{ij} - \log k_j J_{ji})^2 \, . \tag{2'}$$

Thus we minimize the difference between two quantities and Kraut effectively minimizes the difference between the logarithms of these same quantities.

Reference

Kraut, J. (1958). *Acta Cryst.* **11**, 895.

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The crystal structure of tetramethylammonium tetrachlorozincate and tetrachlorocobaltate. (II).

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Introduction

The crystal structure of Cs_2CoCl_4 has been reported by Poraj-Koshitz (1956) and Cs_2ZnCl_4 has been shown to be isomorphous by Brehler (1957). In connection with our study of the configuration of $CuCl_4^{--}$ in $[N(CH_3)_4]_2CuCl_4$ (Morosin & Lingafelter, 1959) it was considered of interest to investigate the corresponding compounds of other bivalent metals. The present report includes the isomorphous pair, $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$.

Experimental

Crystals of both compounds were grown by evaporation at room temperature of aqueous solutions containing the stoicheiometric proportions of $N(CH_3)_4Cl$ and $M^{II}Cl_2$. The crystals of both the colorless zinc compound and the blue cobalt compound were short rod-like prisms bounded by (011) and terminated by (100).

Precession and Weissenberg photographs taken with copper radiation ($\lambda = 1{\cdot}5418$ Å) indicated the two compounds to be isomorphous. The following cell dimensions were obtained; for the zinc compound, results were standardized by superimposing NaCl ($a_0 = 5{\cdot}6280$ Å) photographs on the same films.

	Zincate	Cobaltate
a_0	12·268±0·007 Å	12·24±0·03 Å
b_0	8·964±0·007	8·92±0·02
c_0	15·515±0·012	15·39±0·03

Systematic absences of ($0kl$) for $k+l$ odd and of ($hk0$) for h odd indicate the space group to be *Pnma* or $Pn2_1a$. Number of molecules per cell = 4. Calculated density, 1·38 g.cm.$^{-3}$; observed, 1·34 g.cm.$^{-3}$.

($h0l$) intensity data were collected for $[N(CH_3)_4]_2ZnCl_4$ with an integrating precession camera (Stewart, 1958) using Mo radiation and partial three-dimensional data (i.e., $0kl$ through $6kl$) were collected by means of a non-integrating Weissenberg camera. The number of observed reflections was 540. Intensities were scanned by means of a photometer and relative peak heights were obtained and used as intensities, being placed on an absolute scale by comparison with calculated values at a later stage of the structure determination.

Lorentz and polarization factors were applied and structure factors calculated using Thomas & Umeda (1957) scattering factors. Calculations were carried out on an IBM type 650 computer.

Determination of the structure

The similarity of the axial ratios of the $[N(CH_3)_4]_2ZnCl_4$ (1·368:1·000:1·731) and Cs_2ZnCl_4 (1·317:1·000:1·755; Brehler, 1957) and the identity of their space-group extinctions suggest that the structures are probably similar. Therefore the space group *Pnma* was initially assumed and later verified by the final structure.

A Harker Section $P(x, \frac{1}{2}, z)$ established the positions of the zinc and chlorine atoms. A three-dimensional Fourier synthesis using phases determined by these atoms then established the positions of the nitrogen and carbon atoms. Refinement of both positions and temperature factors proceeded by a few Fourier sections and several difference syntheses. A final over-all Reliability Index of 15·5 was obtained.* For special classes of reflections the indices were:

$h+l = 2n$;	$k = 2n$	14·9
$h+l = 2n$;	$k = 2n+1$	16·7
$h+l = 2n+1$;	$k = 2n$	15·8
$h+l = 2n+1$;	$k = 2n+1$	15·0

The structure exhibited a high temperature factor for the lighter elements and hydrogen atom contributions were not calculated. Atomic positions and individual isotropic temperature factors are listed in Table 1. All atoms are in positions 4*c* except Cl(2), C(3), and C(6), which are in 8*d*.

Table 1. *Atomic positional parameters and temperature factors for* $[\mathrm{N(CH_3)_4}]_2\mathrm{ZnCl_4}$

	x	*y*	*z*	*B*
Zn	0·2460	0·2500	0·4075	4·000
$\mathrm{Cl_1}$	0·0630	0·2500	0·4070	7·400
$\mathrm{Cl_2}$	0·3060	0·0445	0·3400	7·400
$\mathrm{Cl_3}$	0·3130	0·2500	0·5418	8·300
$\mathrm{N_1}$	0·1530	0·2500	0·0975	5·000
$\mathrm{N_2}$	0·4945	0·2500	0·8240	5·500
$\mathrm{C_1}$	0·2770	0·2500	0·0970	8·000
$\mathrm{C_2}$	0·1085	0·2500	0·0020	8·500
$\mathrm{C_3}$	0·1115	0·3910	0·1450	9·000
$\mathrm{C_4}$	0·4405	0·2500	0·7345	8·500
$\mathrm{C_5}$	0·4030	0·2500	0·8935	9·500
$\mathrm{C_6}$	0·5660	0·3910	0·8340	9·000

Discussion

The refinement of the three-dimensional data yielded the expected tetrahedral configuration for the ZnCl_4^{--} ion. Bond lengths and bond angles are given in Table 2.

Table 2. *Bond lengths and angles in* $[\mathrm{N(CH_3)_4}]_2\mathrm{ZnCl_4}$, *with standard deviations*

$\mathrm{Zn{-}Cl_1}$	2·245±0·006 Å	$\mathrm{Cl_1{-}Zn{-}Cl_2}$	109·1±0·22°
$\mathrm{Zn{-}Cl_2}$	2·243±0·006	$\mathrm{Cl_1{-}Zn{-}Cl_3}$	111·7±0·22
$\mathrm{Zn{-}Cl_3}$	2·240±0·006	$\mathrm{Cl_2{-}Zn{-}Cl_3}$	108·3±0·22
$\mathrm{N_1{-}C_1}$	1·521±0·019	$\mathrm{Cl_2{-}Zn{-}Cl_2'}$	110·4±0·22
$\mathrm{N_1{-}C_2}$	1·579±0·019	$\mathrm{C_1{-}N_1{-}C_2}$	109·9±0·97
$\mathrm{N_1{-}C_3}$	1·549±0·019	$\mathrm{C_1{-}N_1{-}C_3}$	109·3±0·97
$\mathrm{N_2{-}C_4}$	1·539±0·019	$\mathrm{C_2{-}N_1{-}C_3}$	109·4±0·97
$\mathrm{N_2{-}C_5}$	1·557±0·019	$\mathrm{C_3{-}N_1{-}C_3'}$	109·4±0·97
$\mathrm{N_2{-}C_6}$	1·546±0·019	$\mathrm{C_4{-}N_2{-}C_5}$	108·3±0·97
		$\mathrm{C_4{-}N_2{-}C_6}$	109·6±0·97
		$\mathrm{C_5{-}N_2{-}C_6}$	109·8±0·97
		$\mathrm{C_6{-}N_2{-}C_6'}$	109·7±0·97

Shorter interionic distances:

$\mathrm{Cl \cdots Cl}$	5·293, 5·523 Å
$\mathrm{CH_3 \cdots CH_3}$	3·515, 3·562
$\mathrm{CH_3 \cdots Cl}$	3·374, 3·509

This structure is very similar to that of $\mathrm{Cs_2ZnCl_4}$ (Brehler, 1957) with the $\mathrm{Cs^+}$ ions being replaced by $\mathrm{N(CH_3)_4^+}$ ions and with each unit-cell edge expanded by a little over 20%.

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References

Brehler, B. (1957). *Z. Kristallogr.* **109**, 68.

Morosin, B. & Lingafelter, E. C. (1959). *J. Amer. Chem. Soc.* To be published.

Poraj-Koshitz, M. A. (1956). *Kristallografya*, **1**, 291.

Stewart, J. M. (1958). Ph.D. Thesis at University of Washington.

Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.

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* The table of calculated and observed structure factors may be obtained from E. C. Lingafelter.

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Crystallographic evidence for the existence of $\mathrm{B_7O}$*.

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Boron can combine with oxygen in different atomic proportions. In addition to the familiar $\mathrm{B_2O_3}$, boron oxides containing less oxygen have been reported in the literature. The existence of the gaseous BO has been proven convincingly (Albrecht & Mallett, 1954), whereas the characterization of a suboxide $\mathrm{B_3O}$ (Kahlenberg, 1925) has been less than satisfactory. This note presents crystallographic evidence of the occurrence of the suboxide, $\mathrm{B_7O}$.

In a preliminary study (Eding, 1956), the brown microcrystalline material which had been obtained from the American Potash & Chemical Corporation was found to contain only traces of nitrogen and magnesium, besides boron and oxygen; its analytical formula was $\mathrm{B_{6\cdot6}O}$. Its X-ray pattern did not agree with that of any of the known boron modifications or of boron oxide, or with any of their combinations. The material appeared to be homogeneous, because partial chemical dissolution did not change the X-ray pattern. These results could be reasonably explained by assuming that the sample was $\mathrm{B_7O}$, contaminated by about 2% of $\mathrm{B_2O_3}$. However, it could also be the suboxides $\mathrm{B_{13}O_2}$ or $\mathrm{B_6O}$ contaminated with boron, or even a new modification of B containing amorphous $\mathrm{B_2O_3}$.

To establish the identity of the material, a quantitative X-ray powder-study was undertaken. With Cu $K\alpha$ radiation, forty-four fairly sharp lines were obtained, some of

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