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Linear Antiferromagnetism in Dichloro(1,2,4-triazole)copper(II) and Copper(II) Benzoate Trihydrate

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The magnetic susceptibilities of dichloro(1,2,4-triazole)copper(II) and copper(II) benzoate trihydrate have been determined in a temperature range of 4.2–300°K. The magnetic susceptibility of the former compound can be expressed as a sum of two terms: a low-temperature paramagnetic contribution of a debatable origin and a linear antiferromagnetism of one-dimensional spin lattices. The former obeys the Curie–Weiss law and is effective at very low temperatures. The latter gives rise to a characteristic temperature dependence of the magnetic susceptibility having a maximum at about 11°K. The energy of antiferromagnetic interaction J/k between the nearest neighbors is equal to -17.9°K . The magnetic behavior of the latter compound is similar to that of the former, the interaction energy J/k being estimated at about -12.7°K .

Introduction

In the crystals of dichloro(1,2,4-triazole)copper(II),¹ each copper atom has a distorted octahedral coordination group consisting of four chlorine and two nitrogen atoms. The structural unit is an infinite chain in which octahedral groups are joined by sharing chlorine edges and are also linked by 1,2,4-triazole molecules with a Cu–Cu distance equal to 3.40 Å. Copper(II) benzoate trihydrate² has an analogous structure: neighboring copper atoms are 3.15 Å distant from each other and are bridged by two oxygen atoms and one Cu–O–C–O–Cu link to form a linear chain. In view of the close distance of approach and the bridging arrangement of copper atoms, one would expect the presence of a strong spin interaction between copper atoms. However, normal magnetic moments have been observed.^{3,4} In order to obtain further information about the magnetic properties of these compounds, we have determined the magnetic susceptibility over a temperature range of 4.2–300°K.

Experimental Section

Dichloro(1,2,4-triazole)copper(II) and copper(II) benzoate trihydrate were prepared and analyzed as described in previous papers.^{3,4}

Above the liquid nitrogen temperature, the magnetic susceptibility was determined by the Gouy method using an Ainsworth recording semimicrobalance, the magnetic field strength being about 10,000 Oe.⁵ The temperature was automatically controlled and determined by means of a copper–constantan thermocouple.

In a temperature range of 4.2–80°K, the Faraday method was employed by use of a torsion balance. The field strength amounted to about 3000 Oe. The accuracy was estimated to be about $\pm 1.5\%$. The temperature was measured within an accuracy of about $\pm 1\%$ using an Allen–Bradley carbon thermometer below about 10°K and a Pt–AuCo thermocouple between 10 and 80°K.

Observed molar susceptibilities have been corrected for diamagnetic contributions^{3,4,6} from ligands (in 10^{-6} cgs emu mol⁻¹):

(1) J. A. J. Jarvis, *Acta Cryst.*, **15**, 964 (1962).(2) H. Koizumi, K. Osaki, and T. Watanabé, *J. Phys. Soc. Japan*, **18**, 117 (1963).(3) M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **3**, 239 (1964).(4) M. Inoue, M. Kishita, and M. Kubo, *ibid.*, **4**, 626 (1965).(5) M. Inoue, M. Kishita, and M. Kubo, *ibid.*, **6**, 900 (1967).

(6) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956.

cupric ion, -11 ; chlorine ion, -26 ; 1,2,4-triazole, -38 ; benzoic acid, -70 ; and water, -13 . The temperature-independent paramagnetism was assumed to be 60×10^{-6} emu mol⁻¹.⁷

Results and Discussion

The magnetic susceptibility of dichloro(1,2,4-triazole)copper(II) increases with decreasing temperature and obeys the Curie–Weiss law excellently above about 40°K as shown in Figures 1 and 2. The Curie constant C_h (the subscript h stands for high temperature) and the Weiss constant θ_h were evaluated as 0.426 emu deg mol⁻¹ and -19.0°K , respectively, from data observed at temperatures between 80 and 300°K in order to eliminate a possible paramagnetic effect at low temperature described below. With further decrease in temperature, the susceptibility increases as shown in Figure 3, passes through a broad maximum at about 11°K and a minimum at about 8°K, and again increases in accordance with the Curie–Weiss law with a Weiss constant $\theta_l = 2.70^\circ\text{K}$ (the subscript l stands for low temperature) and a Curie constant $C_l = 0.0279$ emu deg mol⁻¹.

Kobayashi, *et al.*,⁸ have observed an analogous paramagnetic increase for 2,5-dihydroxy-*p*-benzoquinonato-copper(II) and its derivatives at low temperature. They proposed two effects to account for this behavior: the end effect and the odd or even number effect of spins in a chain. Kadota, *et al.*,⁹ determined the magnetic susceptibility of potassium trifluorocuprate(II) and suggested that a very small amount of magnetically isolated cupric ions can cause this type of an extraneous paramagnetism obeying the Curie–Weiss law at low temperature. Another effect is conceivable, *i.e.*, magnetic interaction between one-dimensional lattices. A simple calculation shows that magnetically isolated Cu²⁺ ions of about 6% can account for this low-temperature paramagnetic behavior. However, analytical data showed practically no deviation from the stoichiometric composition (Calcd: Cu, 31.2. Found: Cu, 31.1). The fluctuation of observed magnetic sus-

(7) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).(8) H. Kobayashi, T. Haseda, E. Kanda, and S. Kanda, *J. Phys. Soc. Japan*, **18**, 349 (1963).(9) S. Kadota, I. Yamada, S. Yoi yama, and K. Hirakawa, *ibid.*, **23**, 751 (1967).

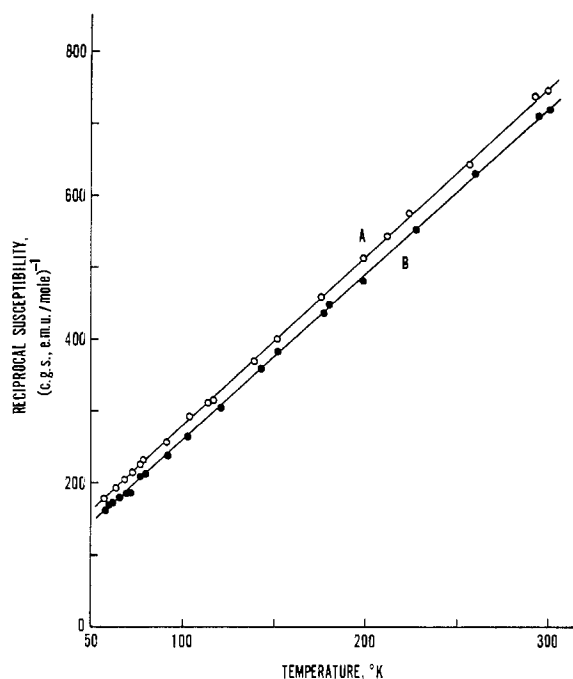


Figure 1.—The reciprocal magnetic susceptibilities (corrected for the temperature-independent paramagnetism) of dichloro-(1,2,4-triazole)copper(II) (A) and copper(II) benzoate trihydrate (B) plotted against the absolute temperature, showing the validity of the Curie-Weiss law at high temperature.

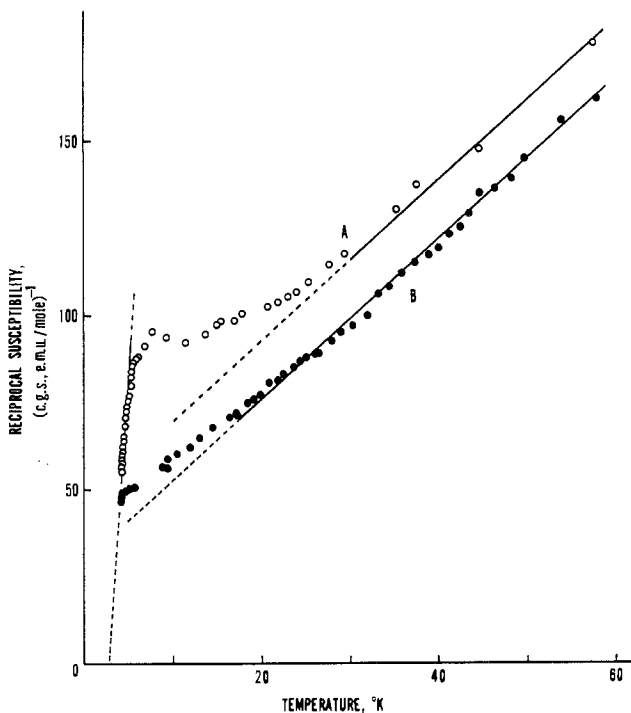


Figure 2.—Plot as in Figure 1, showing deviations from the Curie-Weiss law at low temperature in an expanded scale on both axes.

ceptibilities was less than 1% at room temperature and less than 3% at liquid helium temperature for different samples prepared by the present method of synthesis. The broken curve in Figure 3 shows the susceptibility due to these effects as evaluated by assuming the validity of the Curie-Weiss law. This was subtracted from the

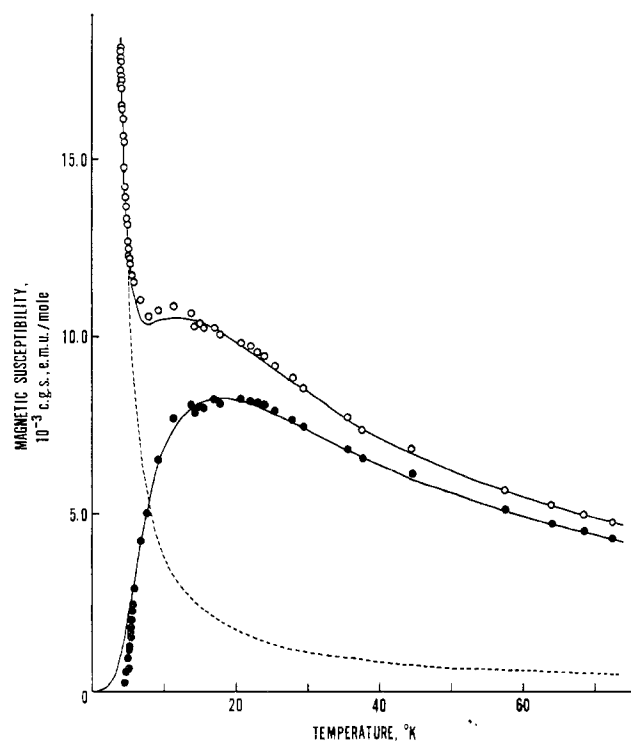


Figure 3.—The observed magnetic susceptibility (O) of dichloro-(1,2,4-triazole)copper(II) resolved into a low-temperature Curie-Weiss curve (broken line) and the linear antiferromagnetism of one-dimensional Ising spin lattices (●).

observed curve and the resulting susceptibility χ' corrected for the low-temperature paramagnetic effect is shown by full circles.

For an infinite one-dimensional Heisenberg spin lattice, the magnetic susceptibility has been calculated as a function of temperature.¹⁰ It shows a broad maximum and tends to a finite value at very low temperature. The observed susceptibility χ as well as χ' does not agree with this theoretical curve.

A theoretical equation has been proposed for the susceptibility χ' of the infinite linear chain of Ising spins.¹¹

$$\chi' = \frac{Ng^2\beta^2}{4kT} \exp\left(\frac{J}{kT}\right) \quad (1)$$

Here J is the energy of exchange interaction between the nearest neighbors, N is the Avogadro number, g is the electronic g factor, β is the Bohr magneton, k is the Boltzmann constant, and T is the absolute temperature. The theoretical curve of χ' plotted against T has a maximum at $T = |J|/k$, below which the susceptibility decreases with decreasing temperature and tends to zero at $T = 0$. Equation 1 can be rewritten as

$$\log\left(\frac{4k}{N\beta^2}\chi'T\right) = 2 \log g + \frac{J}{kT} \quad (2)$$

In Figure 4, observed $\log [(4k/N\beta^2)\chi'T]$ is plotted against $1/T$. The curve is strictly linear except for data at very low temperature. From the slope and the intercept of the straight line, the interaction energy and

(10) J. C. Bonner and M. E. Fisher, *Phys. Rev.*, **135**, A640 (1964); V. L. Ginzburg and V. M. Païn, *Soviet Phys. JETP*, **15**, 131 (1962).

(11) G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).

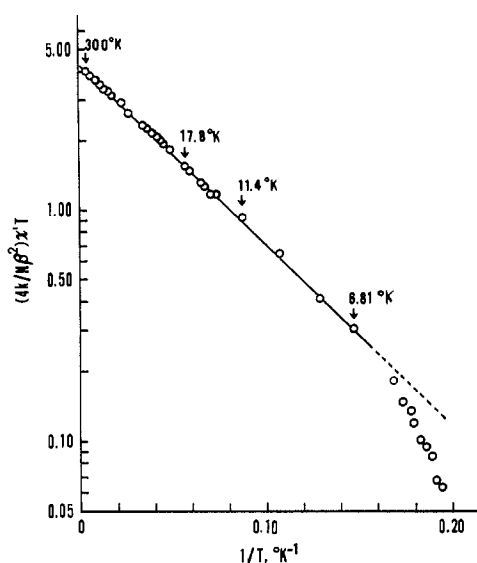


Figure 4.—Semilogarithmic plot of $(4k/N\beta^2)\chi'T$ against $1/T$.

the g factor were evaluated as $J/k = -17.9^\circ\text{K}$ and $g = 2.07$, respectively. Obviously, the deviation from linearity is due to the evaluation of C_1 and θ_1 without paying due regard to the Ising susceptibility χ' . Therefore, the following refinement was made. The theoretical curve (1), which deviates from full circles only below about 6°K , was subtracted from the observed curve, the difference curve being used for the reevaluation of C_1 and θ_1 . Thus, the observed susceptibility χ can be expressed by

$$\chi = \frac{C_1}{T - \theta_1} + \frac{Ng^2\beta^2}{4kT} \exp\left(\frac{J}{kT}\right) \quad (3)$$

with $C_1 = 0.0273 \text{ emu deg mol}^{-1}$, $\theta_1 = 2.54^\circ\text{K}$, $g = 2.07$, and $J/k = -17.9^\circ\text{K}$ as shown by a full curve in Figure 3.

In a high-temperature region such that $|J|/kT \ll 1$, eq 1 leads to

$$\chi' = \frac{Ng^2\beta^2}{4k[T - (J/k)]} \quad (4)$$

Therefore, the Weiss constant θ_h is equal to J/k while the Curie constant C_h is given by $Ng^2\beta^2$, leading to $J/k = -19.0^\circ\text{K}$ and $g = 2.13$ from the high-temperature data in good agreement with the foregoing values (-17.9°K , 2.07) evaluated from the data at lower temperatures. This indicates that the magnetic spins in the copper chains follow the linear Ising model.

It is reported^{12,13} that the magnetic behaviors of copper(II) chloride, bromide, and oxalate obey the linear Ising model above the temperature of the maximum susceptibility and that below this temperature a long-range spin ordering exists. In dichloro(1,2,4-triazole)copper(II), however, short-range magnetic interaction does not lead to any magnetic transition to an ordered state within the temperature range studied, but the theory of linear Ising spins is satisfied.

(12) C. G. Barraclough and C. F. Ng, *Trans. Faraday Soc.*, **60**, 836 (1964).

(13) L. Dubicki, C. M. Harris, E. Kokot, and R. L. Martin, *Inorg. Chem.*, **5**, 93 (1966); B. N. Figgis and D. J. Martin, *ibid.*, **5**, 100 (1966).

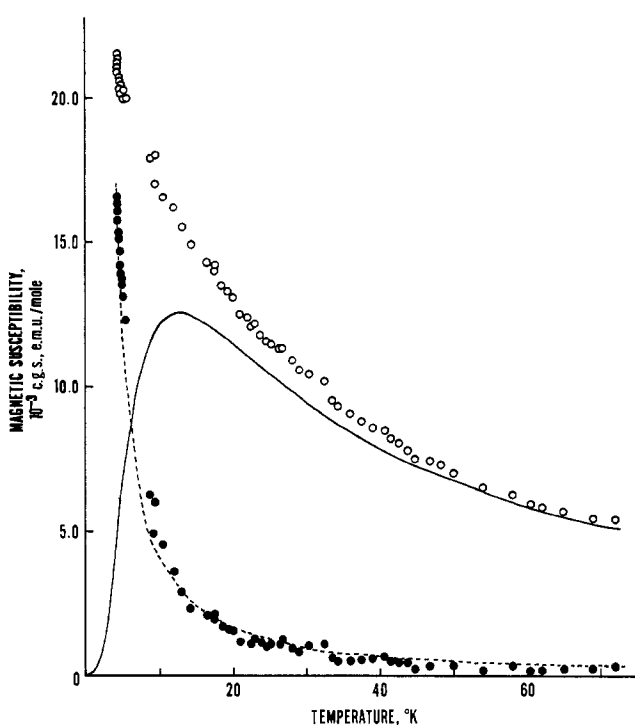


Figure 5.—The observed magnetic susceptibility (O) of copper(II) benzoate trihydrate resolved into a low-temperature Curie-Weiss curve (broken line) and the linear antiferromagnetism of one-dimensional Ising spin lattices (solid line).

The crystal of copper(II) benzoate trihydrate contains isolated linear chains bearing a strong resemblance to those in the crystal of dichloro(1,2,4-triazole)copper(II). Therefore, the magnetic property of copper(II) benzoate trihydrate also is expected to conform to the linear Ising model. In fact, the Curie-Weiss law is obeyed above about 25°K , C_h and θ_h being evaluated as $0.434 \text{ emu deg mol}^{-1}$ and -12.7°K , respectively, from susceptibilities observed at $80\text{--}300^\circ\text{K}$. However, the same method as applied to dichloro(1,2,4-triazole)copper(II) cannot be taken, because the Curie constant and the Weiss constant could not be determined accurately from the low-temperature data owing to the narrow temperature range of the paramagnetic effect. In addition, no definite maximum appeared in the magnetic susceptibility *vs.* temperature curve. Therefore, the following converse procedure was taken tentatively. J/k was assumed to be equal to the high-temperature Weiss constant, -12.7°K , which is in fair agreement with -15°K given by Lewis and Mabbs,¹⁴ while the g value was calculated as 2.15 from the high-temperature Curie constant C_h . The full curve in Figure 5 was calculated with these parameters for the linear Ising spin lattice. It was subtracted from the observed curve to yield full circles shown in Figure 5. The points lie approximately on a Curie-Weiss curve (broken curve) with $C_1 = 0.028 \text{ emu deg mol}^{-1}$ and $\theta_h = 2.6^\circ\text{K}$. This indicates that the magnetic spins in chains behave as in the Ising model and that the estimated interaction energy is adequate.

The spin interaction is stronger in dichloro(1,2,4-

(14) J. Lewis and F. Mabbs, *J. Chem. Soc.*, 3894 (1965).

triazole)copper(II) ($J/k = -17.9$ to -19.0°K) than in copper(II) benzoate trihydrate ($J/k = -12.7^\circ\text{K}$), despite the fact that the Cu-Cu distance of 3.40 \AA in the former is longer than 3.15 \AA in the latter. Therefore, the superexchange interaction rather than the interaction of direct nature is predominant. This conclusion is supported by the existence of spin densities in the

ligand atoms of dichloro(1,2,4-triazole)copper(II).¹⁵ Thus, although normal magnetic moments have been observed for these compounds at room temperature, the spins are not free from one another, but antiferromagnetic interaction exists between neighboring spins in a chain.

(15) M. Inoue and M. Kubo, *Inorg. Chem.*, **5**, 70 (1966).

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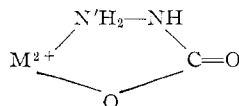
The Nitrogen-Nitrogen Stretching Band in Hydrazine Derivatives and Complexes

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The repulsion between the lone electron pairs of the nitrogen atoms in the staggered hydrazine molecule influences the length of the nitrogen-nitrogen bond; diminution of the repulsion causes shortening of the bond in those derivatives of hydrazine where the lone pair is attracted to bonds. The infrared spectra of several hydrazine derivatives have been examined: the shifts of $\nu(\text{N-N})$ are in agreement with this point of view. The band shifts from 880 toward 1000 cm^{-1} when the repulsion between the lone pairs diminishes. In metal complexes of hydrazine, shifts of the band are also observed, depending on the field effect of the metal cations on the lone pairs, even if the nitrogen-nitrogen bond distance remains unaltered.

The hydrazine molecule $\text{H}_2\text{N-NH}_2$ is composed of two tetrahedra in staggered configuration,^{1,2} one corner in each being occupied by a lone pair. The nitrogen-nitrogen bond distance is $\text{N-N} = 1.46 \text{ \AA}$ in solid hydrazine but it becomes shorter in the cation $^+\text{H}_3\text{N-NH}_3^+$ ($\text{N-N} = 1.40 \text{ \AA}$) and in the cation $\text{H}_2\text{N-NH}_3^+$ ($\text{N-N} = 1.432,^5 1.435 \text{ \AA}$).⁶ This shortening cannot be attributed to increments in π bonding as for diformylhydrazine⁷ but more likely to diminution or suppression of the repulsion between the lone pairs.⁸ Also in chelates of hydrazinecarboxylic acid, $\text{H}_2\text{N}'\text{NHCOOH}$, the bond between nitrogen atoms is shorter ($\text{N-N} = 1.43,^6 1.39,^9 1.40,^{10} 1.43, 1.37,^{11} 1.41^{12} \text{ \AA}$) than in the hydrazine molecule, and again double bonding cannot be invoked to explain the contraction of the bond. As a matter of fact, in the chelate rings



the atoms NH-COO lie in one plane and form a conjugate system, but N' is out of this plane and does not

take part in the conjugation. In these compounds, conjugation of one lone pair with the carboxylato group, accompanied by change of configuration of the nitrogen atom from sp^3 to sp^2 , diminishes the repulsion between lone pairs. On the contrary no such shortening of N-N is observed when the hydrazine molecule behaves as a ligand, either bridging ($\text{N-N} = 1.46 \text{ \AA}$,¹³⁻¹⁵) or unidentate ($\text{N-N} = 1.46 \text{ \AA}$).⁹

The infrared spectra of a large number of hydrazine compounds or derivatives have now been examined in order to confirm these views.

The following sets of compounds have been prepared and examined: (i) compounds containing unidentate N_2H_4 ligands, (ii) compounds containing N_2H_4 bridging groups, (iii) compounds of hydrazinium cations, $\text{H}_2\text{N-NH}_3^+$, and (iv) compounds of hydrazinecarboxylic acid and of hydrazinedithiocarboxylic acid.

Experimental Section

Preparation.—(i) The compounds bis(hydrazine)bis(hydrazinecarboxylato- $\text{N}'\text{,O}$)metal(II), $(\text{N}_2\text{H}_4)_2(\text{H}_2\text{N}'\text{-NH-COO})_2\text{M}^{\text{II}}$, with $\text{M}^{\text{II}} = \text{Co}, \text{Ni},$ or Zn , were prepared from aqueous solutions of salts of the metal, hydrazine hydrate, and carbon dioxide.¹⁶ *Anal.* Calcd for $\text{Co}(\text{N}_2\text{H}_4)_2(\text{H}_2\text{N}'\text{-NH-COO})_2$: N, 41.03; Co, 21.58. Found: N, 40.90; Co, 21.63. Calcd for $\text{Ni}(\text{N}_2\text{H}_4)_2(\text{H}_2\text{N}'\text{-NH-COO})_2$: C, 8.80; H, 5.17; N, 41.06; Ni, 21.51. Found: C, 8.90; H, 5.63; N, 41.00; Ni, 21.35. Calcd for $\text{Zn}(\text{N}_2\text{H}_4)_2(\text{H}_2\text{N}'\text{-NH-COO})_2$: C, 8.59; H, 5.05; N, 40.08; Zn, 23.39. Found: C, 8.81; H, 5.13; N, 39.92; Zn, 23.20.

(ii) (a) The compounds $[\text{M}^{\text{II}}(\text{N}_2\text{H}_4)_2]_n\text{X}_{2n}$, with $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{CH}_3\text{COO}$, were prepared by mixing ammonia, hydrazine hydrate, and salts of

(1) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

(2) A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Acta Cryst.*, **19**, 548 (1965).

(3) R. L. Collin and W. N. Lipscomb, *ibid.*, **4**, 10 (1951).

(4) I. Nitta, K. Sakurai, and Y. Tomiie, *ibid.*, **4**, 289 (1951).

(5) J. H. Bryden, *ibid.*, **11**, 31 (1958).

(6) A. Braibanti, A. M. M. Lanfredi, and A. Tiripicchio, *Z. Krist.*, **124**, 335 (1967).

(7) Y. Tomiie, *Acta Cryst.*, **11**, 774 (1958).

(8) R. C. Johnson, "Introductory Descriptive Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1966, p 68.

(9) A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Z. Krist.*, **122**, 259 (1965).

(10) A. Braibanti, A. Tiripicchio, A. M. M. Lanfredi, and F. Bigoli, *ibid.*, in press.

(11) A. Braibanti, A. Tiripicchio, A. M. M. Lanfredi, and M. Camellini, *Acta Cryst.*, **23**, 248 (1967).

(12) A. Braibanti, A. M. M. Lanfredi, A. Tiripicchio, and F. Bigoli, *ibid.*, in press.

(13) A. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Cryst.*, **16**, 498 (1963).

(14) A. Ferrari, A. Braibanti, G. Bigliardi, and F. DallaValle, *Z. Krist.*, **119**, 284 (1963).

(15) A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Acta Cryst.*, **18**, 367 (1965).

(16) A. Braibanti, G. Bigliardi, and R. C. Padovani, *Gazz. Chim. Ital.*, **65**, 877 (1965).