spectra. If one of the Fe atoms were assumed to be coordinated with both σ-bonded nitrogens and the other with both π-bonding systems of the two acrylonitrile molecules, the observed infrared frequencies would be too high in the former case and too low in the latter case (Table III). The observed three CO-stretching frequencies are in fact just intermediate as expected for the suggested structure.

The nmr spectrum also supports the proposed structure showing a system of bands with a strong band 2.3 ppm downfield from $Si(CH_3)_4$. Detailed considerations of this molecule must await a more thorough structural investigation by X-ray analysis.

Acknowledgment.—We are pleased to acknowledge very helpful discussions with Dr. Heinz Haas.

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The Crystal Structure of Trisilver Dinitrate Tris(acetylacetonato)nickelate(II) Monohydrate[1]

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The structure of trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate, $AgNi(C_5H_7O_2)_3 \cdot 2AgNO_3 \cdot H_2O$, was determined by three-dimensional, single-crystal X-ray diffraction techniques. There are four molecules per unit cell of symmetry $P4_1$ with dimensions $a = b = 15.053 \pm 0.005$ A and $c = 10.800 \pm 0.007$ A. The compound may be considered to be a complex of silver with the tris(acetylacetonato)nickelate(II) ion. The silver ions are apparently bonded to the central carbon atom (the "active methylene") of one chelate ring and to the oxygen atom of an adjacent ring. The average distances for the interactions of the three nonequivalent silver ions are Ag–C = 2.34 ± 0.09 A and Ag–O = 2.46 ± 0.07 A. The nickel ion is octahedrally surrounded by oxygen atoms at an average distance of 2.04 ± 0.06 A and an average O–Ni–O bond angle of 90 ± 3°. Tris(acetylacetonato)nickelate(II) ions are held together by one of the silver ions in spiral chains parallel to the z axis. These spiral chains are in turn held together by the remaining silver ions through connecting nitrate groups. The magnetic moment of the nickel ion is 3.13 BM.

Introduction

A number of reports concerning the crystal structure of metal acetylacetonates and structures involving metal–olefin bonding have appeared in the literature. We have been interested in the various possible configurations of silver ions in metal–olefin complexes and assumed that $AgNi(acac)_3 \cdot 2AgNO_3 \cdot H_2O$ would be of this type. The silver ion appears to be directly bonded to the electron pair of the "active methylene" carbon, Ag–C = 2.34 A, and not to the adjacent carbon atoms, Ag–C = 2.81 A. This geometry suggests a situation similar to the platinum interactions with the "active methylene" carbon[2] of β-diketones. The silver–carbon interaction is probably predominantly ionic. The synthesis and physical properties of this compound and disilver perchlorate bis(acetylacetonato)copper(II) were brought to our attention by Professor Kline.[3] The structure of the copper complex will be described in a later article.

Experimental Section

Crystal.—Bis(acetylacetonato)nickel(II) was prepared by the addition of a solution of nickel(II) chloride to a mixture of water and 2,4-pentanedione containing enough ammonium hydroxide to make them miscible. The resulting crystals were then purified by recrystallization from hot toluene. The crystal structure of bis(acetylacetonato)nickel(II) has been reported[4] and shows that the molecules exist as trimers.

Trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate was prepared by the addition of bis(acetylacetonato)-nickel(II) to a 1.5 *N* aqueous solution of silver nitrate. The blue-green crystals of $AgNi(acac)_3 \cdot 2AgNO_3 \cdot H_2O$ were then recovered by filtration and appeared as elongated parallelepipeds. Crystals suitable for X-ray diffraction studies were difficult to obtain since the compound could not be recrystallized.

Anal. Calcd for blue-green complex: Ag, 39.43; Ni, 7.14; acac, 36.14. Found:[3] Ag, 39.08; Ni, 7.25; acac, 36.3.

A second compound of proposed formula $AgNi(acac)_3 \cdot AgNO_3 \cdot H_2O$ was obtained if 0.5 *N* aqueous solutions of silver nitrate was used. The crystals were blue.

Anal. Calcd for blue complex: Ag, 33.10; Ni, 9.01; acac, 45.61. Found:[3] Ag, 32.9; Ni, 9.11; acac, 46.7.

A single crystal of the blue-green di(silver nitrate) complex, with dimensions of 0.25 × 0.25 × 1.35 mm, $\mu R = 0.58$, was selected for X-ray measurements. The crystal was sealed in a Pyrex capillary to retard decomposition. Upon repeated exposure to light and X-rays, the crystal turned brown around the edges indicating some decomposition. Single crystals of the blue complex decomposed rapidly at room temperature upon exposure to X-rays, and no reliable intensity data were collected.

X-Ray Data.—All data used for intensity measurements were obtained at room temperature with the multiple film (three films) equiinclination Weissenberg technique. Reflections ($hk0$) to ($hk6$) were recorded using filtered copper radiation, $\lambda_{CuK\alpha}$ 1.54180. The intensities were visually estimated by comparison

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[1] This work was supported by a grant from the Robert A. Welch Foundation.

[2] (a) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.* (London), **A254**, 205 (1960); (b) A. C. Hazell and M. R. Truter, *ibid.*, **A254**, 218 (1960); (c) A. G. Swallow and M. R. Truter, *ibid.*, **A266**, 527 (1962); (d) A. Robson and M. R. Truter, *J. Chem. Soc.*, 630 (1965).

[3] R. K. Kline, private communication.

[4] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

with calibration strips prepared from a suitable reflection of the crystal under investigation. The intensity of each reflection was read at every occurrence on the three films, and the values were averaged. A total of 926 independent reflections was recorded. Lorentz polarization and absorption corrections, using the values of Bond,[5] were made with the aid of an IBM 1620 computer. The intensities from the various layers were initially scaled together by a statistical procedure and later by comparison of the observed and calculated structure factors.

Powder lines of sodium chloride were superimposed upon several of the Weissenberg photographs. The linear dimensions of the film were calibrated by a least-squares procedure utilizing the powder lines. A number of high-angle reflections from the single-crystal pattern were then read, and a least-squares procedure was used to calculate the cell dimensions. The unit cell dimensions from three representative single crystals were determined by this procedure and the values were averaged. This was necessary since the same crystal was not used for intensity and unit cell measurements, and slight variations in dimensions were observed.

The unit cell was found to be tetragonal with dimensions $a = b = 15.053 \pm 0.005$ A and $c = 10.800 \pm 0.007$ A. The calculated density for four molecules per unit cell was 2.235 g/cm^3; the observed density was 2.18 g/cm^3. Precession, cone axis, rotation, and powder photographs were taken with both copper and molybdenum radiation. The symmetry and extinctions ($00l$, $l = 4n$) were consistent with space group $P4_1$ and its enantiomorph $P4_3$. Space group $P4_1$ was chosen.

Magnetic Susceptibility.—The magnetic susceptibilities were measured by the Faraday method at two different field strengths. $Hg[Co(CNS)_4]$ was used as a calibration standard. The effective magnetic moment was calculated by the formula $\mu_{\text{eff}} = 2.84\sqrt{\chi_M^{\text{cor}}T}$, where χ_M^{cor} is the corrected magnetic moment per Ni(II) ion. All appropriate diamagnetic corrections were made.[6]

Determination of Structure

The coordinates of the silver and nickel atoms were obtained from a three-dimensional Patterson map. The "z" coordinates are not fixed by the space group, and the "z" coordinate of one silver ion was arbitrarily chosen. The phases of 792 reflections were determined by computing structure factors utilizing the coordinates of these heavy atoms, and a three-dimensional electron density map was calculated. A set of peaks with approximate octahedral symmetry surrounded the nickel ion and was assumed to be oxygen atoms. Several additional peaks were tentatively identified as carbon atoms. The nitrate ions and the majority of the carbon atoms were not resolved.

Sixteen atoms were used in a least-squares refinement to obtain a better set of phases for computing a second three-dimensional electron density map. A full-matrix, least-squares program by Gantzel, Sparks, and Trueblood, written for the IBM 7090, was modified for the Control Data 3600. After six cycles with isotropic temperature factors, the R value dropped from 0.28 to 0.16. A second three-dimensional electron density map was computed. A number of peaks occurred to which a proposed model of the molecule could be fitted. An oxygen atom associated with a water of hydration, not previously reported in the chemical analysis, was observed. Resolution of the nitrate ions and the carbon atoms most closely associated with the silver ions was poor.

TABLE I

ATOMIC PARAMETERS

	x/a	y/a	z/c	B
Ag(1)	0.4816 (5)[a]	0.0625	0.4317 (0)	3.9 (1)
Ag(2)	0.4561 (6)	0.3172	0.9097 (8)	4.5 (1)
Ag(3)	0.1653 (6)	0.0597	0.993 (1)	5.2 (2)
Ni	0.3987 (8)	0.1186	0.115 (1)	2.7 (2)
O(1)	0.419 (4)	0.240	0.209 (6)	4.3 (3)
O(2)	0.314 (4)	0.081	0.248 (7)	2.4 (3)
O(3)	0.503 (3)	0.061	0.198 (7)	2.6 (3)
O(4)	0.484 (4)	0.164	0.983 (8)	2.5 (3)
O(5)	0.297 (3)	0.169	0.003 (7)	3.3 (3)
O(6)	0.384 (3)	0.999	0.035 (7)	2.7 (3)
O(7)	0.445 (5)	0.311	0.663 (9)	5 (1)
O(8)	0.375 (8)	0.415	0.747 (10)	8 (2)
O(9)	0.369 (7)	0.382	0.536 (10)	8 (2)
O(10)	0.117 (11)	0.993	0.555 (22)	12 (2)
O(11)	0.127 (9)	0.962	0.739 (10)	6 (1)
O(12)	0.167 (10)	0.080	0.726 (15)	11 (2)
H_2O	0.482 (5)	0.225	0.438 (7)	5.1 (3)
C(1)	0.375 (6)	0.308	0.151 (7)	3.1 (4)
C(2)	0.340 (5)	0.312	0.041 (7)	2.1 (4)
C(3)	0.289 (6)	0.252	0.991 (9)	2.8 (4)
C(4)	0.405 (7)	0.392	0.220 (10)	4.1 (5)
C(5)	0.223 (8)	0.275	0.889 (9)	5.4 (5)
C(6)	0.554 (9)	0.115	0.970 (9)	4.4 (4)
C(7)	0.606 (8)	0.005	0.036 (9)	3.4 (4)
C(8)	0.572 (7)	0.021	0.145 (9)	4.0 (4)
C(9)	0.146 (8)	0.388	0.610 (9)	6.1 (5)
C(10)	0.617 (6)	0.964	0.142 (9)	3.5 (4)
C(11)	0.247 (5)	0.031	0.230 (6)	2.5 (3)
C(12)	0.240 (5)	0.968	0.129 (6)	3.2 (3)
C(13)	0.310 (6)	0.949	0.041 (7)	3.1 (3)
C(14)	0.303 (8)	0.868	0.956 (9)	5.1 (5)
C(15)	0.202 (9)	0.030	0.362 (9)	8.3 (9)
N(1)	0.396 (5)	0.367	0.634 (9)	2.1 (4)
N(2)	0.136 (8)	0.014	0.659 (10)	3.1 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The standard deviations for the x and y coordinates are identical.

Four oxygen atoms associated with the two nitrate ions were still difficult to locate and were temporarily omitted. Six least-squares cycles were carried out utilizing 30 atoms and isotropic temperature factors. The R factor dropped to 0.14. Tentative parameters for the remaining four oxygen atoms were then introduced, and eight additional least-squares cycles were carried out. The R value was 0.12 at the end of these calculations. A detailed analysis of the structure and standard deviations of the atomic parameters discouraged further computations with the intensity data that were available. When automatic diffractometer equipment becomes available, an attempt will be made to find a more suitable crystal. Low-temperature techniques will also be employed, and some statement concerning systematic errors due to absorption can be made.

The final parameters are listed in Table I along with the estimated standard deviations. The standard deviations of most bonds are quite large, but the bond lengths averaged over all three rings give values in good agreement with those in the literature. All averaged bond lengths are given in Table II. A listing

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(5) W. L. Bond, "International Tables for Crystallography," Vol. 2, The Kynoch Press, Birmingham, England, 1959.

(6) B. N. Figgis and J. Lewis, "Technique of Inorganic Chemistry," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1965, p 142.

Table II

Interatomic Distances (A)

Ag–O	2.46 ± 0.07[a]
Ag–C (methylene carbon)	2.34 ± 0.09
Ag–C (adjacent carbons)	2.81 ± 0.08
Ni–O	2.04 ± 0.06
C–O	1.30 ± 0.08
C–C	1.38 ± 0.10
C–CH_3	1.54 ± 0.05
N–O	1.24 ± 0.11

[a] Standard deviations are calculated for the average values of the bond lengths. These are frequently less than the standard deviation for an individual bond length.

of observed and calculated structure factors, on an absolute scale, are given in Table III.

Discussion

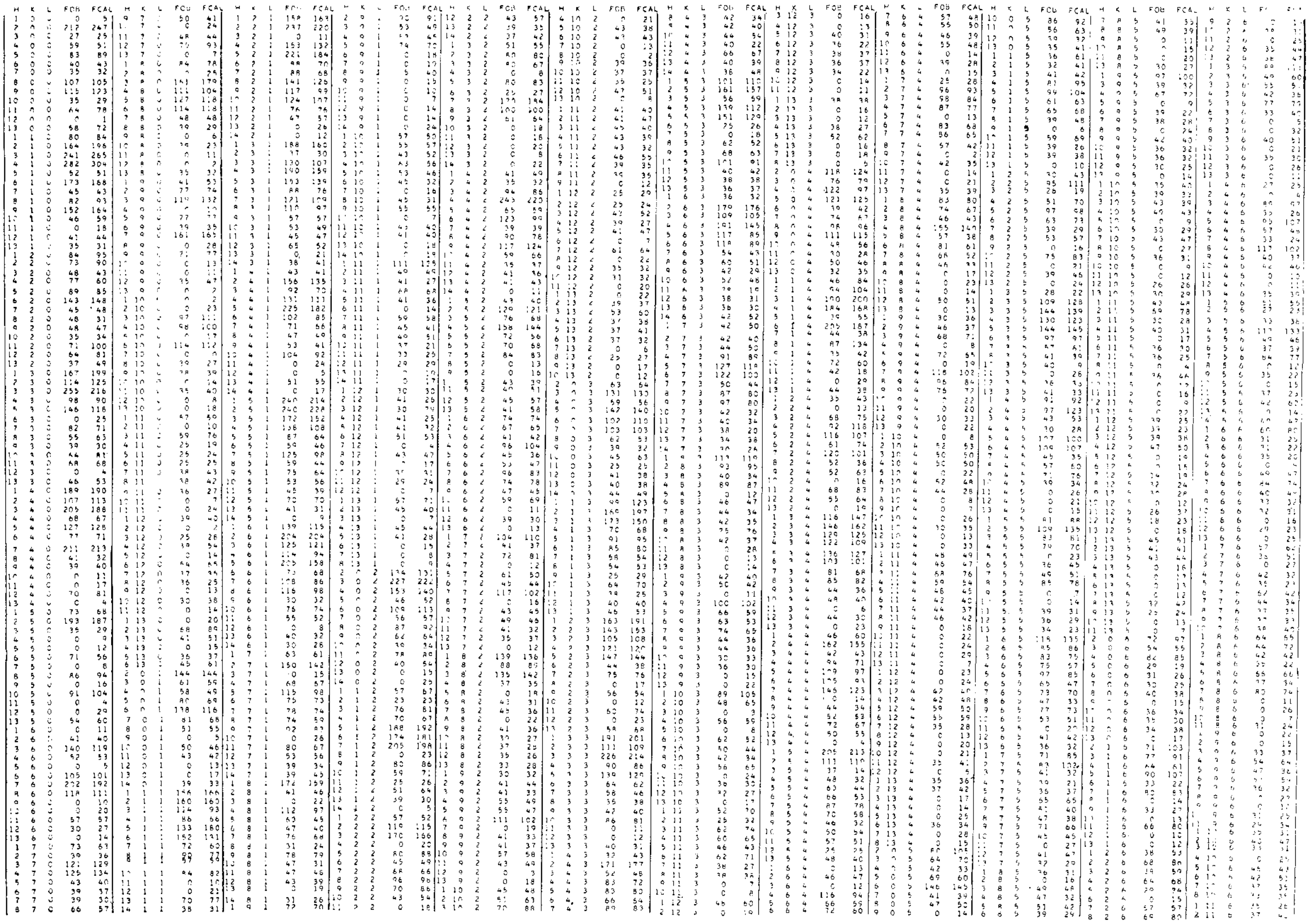
The structure of trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate is shown in Figure 1. The oxygen atoms of the acetylacetonate groups are arranged in an octahedral configuration around the central nickel ion. An axis in the "*Z*" direction passing through the nickel ion is of almost trigonal symmetry. The Ni–O bond distances average 2.04 ± 0.06 A, and the O–Ni–O bond angle is 90 ± 3°. The average values of bond distances and angles around the chelate ring are shown in Figure 2. These values are consistent with previous structural work on metal acetylacetonate systems.

Each silver ion is approximately tetrahedrally surrounded by three oxygen atoms and one carbon atom. The silver ions are much closer to the central carbon atom in the chelate ring, 2.34 ± 0.09 A, than either adjacent carbon atom, 2.81 ± 0.08 A. This can be interpreted as an interaction of the silver ion with the electron pair on the "active methylene" carbon similar to that found with platinum.[2] The C–C–Ag bond angles average 96 ± 6°. The Ag–C bond possibly has considerable ionic character. If the ionic radius of Ag^+ is assumed to be 1.26 A, then the ionic radius of the "active methylene" carbon would be 1.08 A. This is a reasonable value for the ionic radius of a "carbanion."

The silver ions are bonded also to an oxygen atom of an adjacent chelate ring but in the same molecule. This results in the chelate ring being bent about 19° along a line through the two chelate oxygen atoms. By analogy to bis(acetylacetonato)nickel(II),[4] one might expect that the oxygen atoms bonded to both nickel and silver ions might have slightly longer Ni–O bond lengths than those bonded to nickel alone. The errors in individual bond lengths preclude any analysis of small differences.

Table III

Observed and Calculated Structure Factors



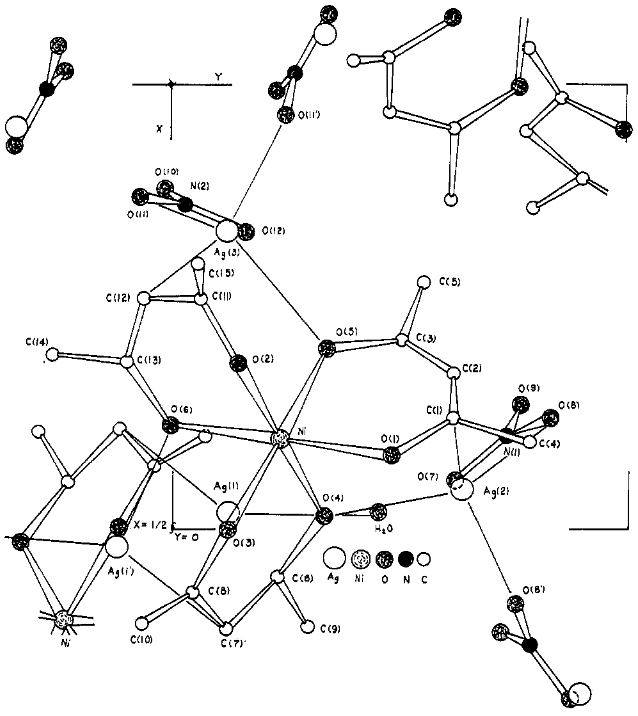


Figure 1.—Projection of one complete molecular unit and environment onto (001).

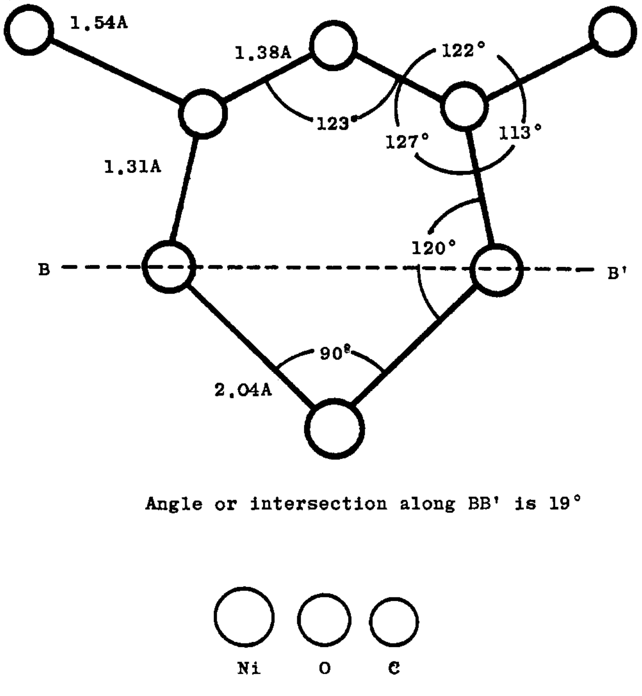


Figure 2.—Averaged molecular dimensions of the coordinated acetylacetone ligands in the tris(acetylacetonato)nickelate(II) ion.

Silver ion (1) is considered to be the unique silver ion in the structure. It binds the tris(acetylacetonato)-nickelate(II) ions together in spiral chains parallel to the *Z* axis. The other silver ions are bound to the tris-(acetylacetonato)nickelate(II) ion and to two nitrate ions. The nitrate ions are in turn bound to the silver ions associated with other tris(acetylacetonato)nickelate(II) ions. These silver and nitrate ions form spiral chains parallel to the *Z* axis and bind the chains of silver tris(acetylacetonato)nickelate(II) together. The nitrate ions are approximately planar with N–O = 1.24 ± 0.11 A and O–N–O = 122 ± 12°.

The water molecule completes the coordination sphere of Ag(1) and aids in binding the molecules together. The water molecule is probably hydrogen bonded to oxygen O(1), 2.66 A, of the chelate molecule directly beneath in the adjacent unit cell. It may also be within hydrogen-bonding distance of oxygen O(7), 2.81 A, of the nitrate group.

The effective magnetic moments of both the di-(silver nitrate) and mono(silver nitrate) compounds are listed in Table IV. The data appear to follow a Curie–Weiss dependence, θ = 10°K, but the limited amount of data does not justify this correction. The magnetic moments of the two compounds are essentially identical indicating similar chemical environments, and the magnitudes are consistent with octahedral symmetry. No electron spin resonance spectrum was obtained at 1.7°K.

TABLE IV

EFFECTIVE MAGNETIC MOMENTS (μ_{eff} IN BOHR MAGNETONS)

Temp, °K	AgNi(acac)$_3$·2AgNO$_3$·H$_2$O	AgNi(acac)$_3$·AgNO$_3$·H$_2$O
273	3.13	3.10
201	3.13	3.12
77	3.05	2.99

There are a number of features of the structure of trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate which make the selection of a crystal for intensity measurements quite important. Only two oxygen atoms of each nitrate group are bonded, allowing the nitrate ion considerable thermal motion in the crystal. Both silver nitrate units are not simultaneously required to bind the silver tris(acetylacetonato)-nickelate(II) chains together. Nonstoichiometric ratios are then possible, and care must be taken in the preparation of the compound. The absence of a silver nitrate unit would allow the bent chelate ring to achieve a more planar configuration and also result in more disorder and thermal motion in the nitrate groups adjacent to the missing unit. When automatic single-crystal diffraction equipment becomes available, a number of carefully prepared crystals will be screened for use in accurate low-temperature intensity measurements.

The mono(silver nitrate) compound does not have the structure of the di(silver nitrate) compound with half of the silver nitrate units randomly missing. This might seem logical when the instability of the mono-(silver nitrate) compound and the formation of nonstoichiometric ratios are considered.

Acknowledgment.—We wish to express our appreciation to Dr. E. A. Meyers for aid in some of the computations and to Mr. M. R. Kidd for the magnetic susceptibility data.