Figure 5. ^{115}In chemical shifts as a function of total ligand electronegativity for $InX_nY_{4-n}^-$ and InX_2YZ^- anions. Key numbers refer to entries in Table IV.

the data in Figure 5 generally confirm such a model. The curves are nonlinear, and markedly so for the chloride–iodide complexes, so that in any given series, an $InX_nY_{4-n}^-$ complex has a lower chemical shift than would be estimated by interpolation from the appropriate InX_4^-/InY_4^- pair results on the assumption of a linear dependence of δ on $\sum\chi$. The results for InX_2YZ^- anions show similar general trends, and the set $InClBr_3^-$, $InClBr_2I^-$, $InClBrI_2^-$, $InClI_3^-$ lie on a smooth curve. All in all, it is obvious that factors over and above ligand electronegativity are involved in determining δ, demonstrating that the ionic model is not a completely accurate description of the bonding. As expected, the effects of a significant covalent contribution show up most clearly in anions containing In–I bonds. We hope to discuss this point more fully elsewhere.

Finally we note that these NMR results cast an interesting light on the earlier preparative and spectroscopic work. First, insofar as the solution chemistry is concerned, the behavior of a mixture of InX_4^- anions is identical with that of the corresponding $InX_nY_{4-n}^-$ anion, so that the elaborate preparative route was probably unnecessary in such cases, although it may have merit elsewhere. Second, we have shown that a sample of $[(C_4H_9)_4N][InCl_3Br]$ of known vibrational spectrum dissolves in ethanol to give a five-line ^{115}In NMR spectrum, which is not significantly changed by raising of the temperature. On crystallization, the $InCl_3Br^-$ salt is again obtained, and the residual liquor still shows a five-line spectrum. Thus the present work and that described earlier[23] are experimentally compatible, and all that remains is to find a satisfactory explanation. Work on this is proceeding.

Contribution from the Department of Chemistry,
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The Cluster Approach to Exchange Coupling in Diamminecopper(II) Carbonate, Cu(NH$_3$)$_2$CO$_3$

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The layer structure of $Cu(NH_3)_2CO_3$ consists of carbonate-bridged chains of copper(II) ions linked together into sheets by hydrogen bonding. The susceptibility data for this magnetically condensed compound have been analyzed by using a cluster approach in which the two different kinds of exchange-coupling interactions were included explicitly. Clusters of six copper ions give the best representation of the experimental data, with the intrachain coupling constant being -5.2 cm^{-1} and the interchain coupling constant being -2.6 cm^{-1}.

Introduction

The magnetic properties of exchange-coupled polymeric compounds such as chains or sheets can be calculated only for a limited number of cases. These include the Ising chain, the XY chain, the Ising sheet, and the Heisenberg chain with infinite spin.[2a] In other cases the approach that has been taken in the calculations is illustrated by the work of Bonner and Fisher[2b] on the Heisenberg chain with $S = \frac{1}{2}$. They carried out exact calculations on small rings and short chains of $S = \frac{1}{2}$ ions and extrapolated their results to the limit of an infinite one-dimensional chain to obtain an approximation for the magnetic properties at that limit. Weng[3] followed Bonner and

Fisher's cluster approach in his calculations of the magnetic properties of Heisenberg chains with $S \geq 1$. Recently the magnetic properties of linear Heisenberg chains with nearest- and next-nearest-neighbor exchange[4] and of alternating Heisenberg chains[5] have also been investigated by using the cluster approach.

The recent reevaluation of the magnetic data for Cu-(NH$_3$)$_2$CO$_3$ from this laboratory[6] by Kamase, Osaki, and Uryū[7] was based on a misinterpretation of the published data.

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(3) Weng, C.-Y. Ph.D. Dissertation, Carnegie-Mellon University, 1968.
(4) Ananthakrishna, G.; Weiss, L. F.; Foyt, D. C.; Kelin, D. J. *Physica B+C (Amsterdam)* **1976**, *81B+C*, 275.
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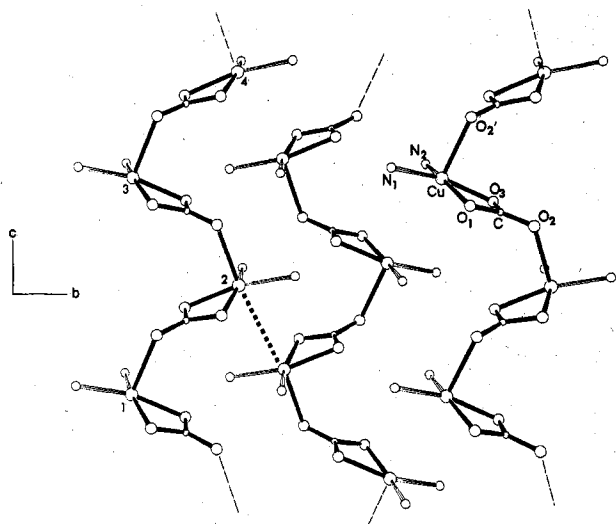(7) Kamase, K.; Osaki, K.; Uryū, N. *Inorg. Chem.* **1978**, *17*, 2958.

Figure 1. Structure of $Cu(NH_3)_2CO_3$ projected onto the bc plane showing the chain of square pyramidally coordinated copper ions.

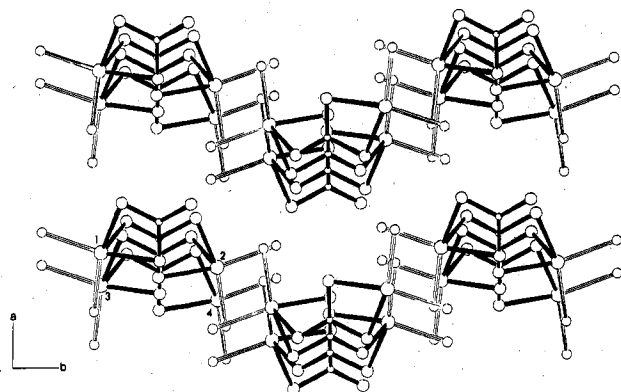**Figure 2.** Structure of $Cu(NH_3)_2CO_3$ projected onto the ab plane (down the chain direction) showing the isolated layers of interacting chains.

This problem has led us to evaluate the applicability of the cluster approach to exchange in this lower symmetry and relatively complex system. The results of our studies are discussed in this article.

Results and Discussion

(a) **Structure.** The structure of $Cu(NH_3)_2CO_3$ was described most recently by Meyer et al.[8] in 1972. The structure is complicated and consists of infinite chains of square pyramidally coordinated copper ions which are held together by hydrogen bonds to form well-defined layers in the bc plane. The coordination to copper in the basal plane of the square pyramid is by the two ammines and a bidentate carbonate ion. The chain is propagated through coordination by the third carbonate oxygen to an adjacent copper. This third oxygen occupies the apical position of the next square pyramidally coordinated copper ion. The structure of a segment of one layer is shown in Figure 1. The base of each square pyramid in one chain lies parallel to the base of a square pyramid in a neighboring chain with a Cu–Cu separation of 3.5 Å, with the result that copper ions in one chain are only close to alternate copper ions on adjacent chains as shown in Figure 1. The intrachain and interchain interactions lead to a two-dimensional network of roughly parallel sheets as shown in the view along the c axis in Figure 2. The magnetic problem may then be described as a two-dimensional array of ex-
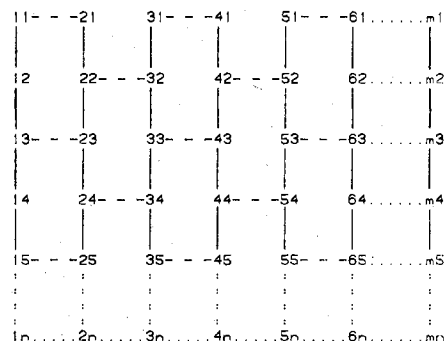
(8) Meyer, M. H.; Singh, P.; Hatfield, W. E.; Hodgson, D. J. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1607.

Figure 3. Possible exchange interactions in $Cu(NH_3)_2CO_3$. Solid lines represent intrachain interactions and dashed lines represent interchain interactions, there being M chains with N copper atoms in each chain.
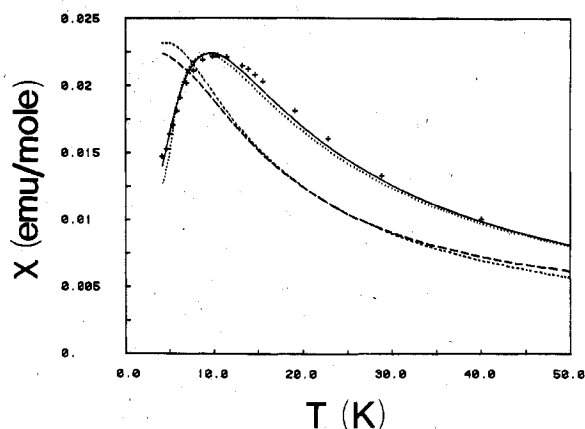

Figure 4. Best fits of the experimental data to the six-copper cluster models: —, alternating chain with Θ; ···, array 3; - - -, array 1; — — —, array 2. Parameter values are given in Table I.

change-coupled chains of $S = \frac{1}{2}$ copper ions with the exchange-coupling pathways which are shown schematically in Figure 3. In Figure 3, the solid lines depict the carbonate-bridged copper ions in chains, and the dotted lines indicate interchain copper–copper interactions. It is important to note that these latter interactions are through-space interactions; i.e., there are no intervening bridging ligands to supply pathways for superexchange.

(b) **Magnetic Data.** The magnetic data on $(NH_3)_2CuCO_3$ was published some years ago by Jeter et al.[6] These data are shown as the experimental points in Figure 4. The best fit to the susceptibility at the time was with a modified dimer model, eq 1, with $J = -4.5$ cm⁻¹ and Θ (to take account of

$$\chi_m = \frac{Ng^2\beta^2}{3k(T - \Theta)}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} \quad (1)$$

the nondimer interactions in the chainlike structure) $= -1.9$ K, i.e., antiferromagnetic in nature. Both negative J and Θ values are reflected by a clear maximum in the susceptibility at 11 K.

Jeter et al.[6] also included in their paper a figure showing the calculated magnetization expected if all the "dimeric molecules" were in a triplet state. These calculated values were presented as a function of H/T. The object of the calculation was to determine if the compounds were more easily magnetized than spin $S = 1$ systems. The results of the calculation indicated that such was the case, and it was concluded that the antiferromagnetic interactions in $Cu(NH_3)_2CO_3$ arose from both interchain and intrachain effects.

Recently, Kamase et al.[7] have suggested that two versions of a tetramer model for this compound give a better account of the experimental data. In one of their tetramer models both
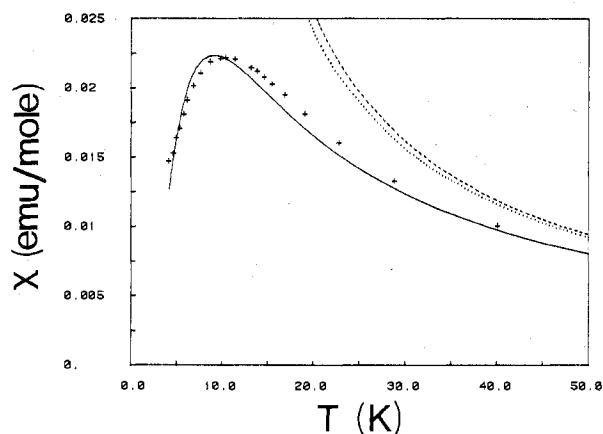
Figure 5. Best fit of the experimental data to the four-copper cluster models: —, best fit (array 4); ⋯, $J_1 = 2.52$ cm^{-1} and $J_2 = 2.34$ cm^{-1}; ---, $J_1 = 1.0$ cm^{-1} and $J_2 = -2.0$ cm^{-1} ($\Theta = 1.5$ K from ref 7).

exchange interactions were ferromagnetic, while in the other model two exchange interactions were ferromagnetic while a third interaction was antiferromagnetic. These analyses of Kamase et al.[7] were based on the calculated magnetization data of Jeter et al.,[6] not the experimental data. Further, the maximum in susceptibility certainly cannot be reproduced by a model containing only ferromagnetic interactions in an applied magnetic field of only 1 T. The failure of the analysis by Kamase et al.[7] to account for the susceptibility data is clearly shown by the lines in Figure 5 which were calculated from their tetramer model and their parameters.

(c) Formulas and/or Series Expansions for Magnetic Susceptibility. One method of analyzing the magnetic susceptibility data of compounds forming extended lattices is to use explicit formulas or series expansions. These methods rely on high symmetry; i.e., there is normally only one type of interaction represented by an exchange-coupling constant J, and this interaction is propagated in a regular manner throughout the lattice. This is clearly not the case for $Cu(NH_3)_2CO_3$, since the structure, which is shown in Figure 1, indicates that there are two different kinds of interactions, one of these being an intrachain superexchange interaction via the carbonate bridge and the second one being an interchain interaction which is a through-space interaction. Consequently, it is not surprising that none of the Heisenberg models for which expansions are available (chain, two-dimensional lattice, etc.) are capable of describing the magnetic data. (Copper(II) is not an Ising-like ion, and so the Ising model was not considered in the present work. Jeter et al.[6] had shown that the Ising chain was inadequate to explain the data.) Obviously, a cluster approach would be expected to be more realistic, because in such an approach the symmetry of the particular lattice can be accounted for explicitly.

(d) The Cluster Approach. The use of results calculated for small clusters to model the magnetic properties of extended lattices was briefly reviewed in the Introduction. The calculational problem can be divided into two parts. First, the eigenvalues of the interaction Hamiltonian are determined, and second, the susceptibility is generated by considering the interaction of the cluster with the magnetic field. For small clusters, the eigenvalues can often be determined analytically, and for the specific case of copper(II) with $S = \frac{1}{2}$ this has been done for tri- and tetraspin $\frac{1}{2}$ cases.[9] However, even for the $S = \frac{1}{2}$ tetraspin case there are several combinations of exchange parameters (e.g., the most general case with no symmetry among the interactions) for which it is impossible

to obtain analytic expressions for the eigenvalues.[9] For these low-symmetry cases, and for many larger cluster sizes, it is necessary to use numerical methods. We have now been able to generate a completely general computer program which allows the calculation of susceptibility and magnetization as a function of temperature *and applied magnetic field strength* for *any* number of copper atoms in *any* array considering *any* number of pairwise interactions. (We assume a pairwise interaction of the form $-2\sum_k J_k \sum_{i \geq j} \hat{S}_i \cdot \hat{S}_j$.) The only limit in the calculation is in computer size.

The calculations are done in the following way. The N electron wave functions for an N copper system are generated by using a binary counter: (0) $S_z = +\frac{1}{2}$ and (1) $S_z = -\frac{1}{2}$, where all possible combinations lead to the 2^N wave functions. The pairwise interaction matrix based on $-2\hat{S}_1 \cdot \hat{S}_2$ is then generated and stored. The complete $2^N \times 2^N$ matrix under the interaction Hamiltonian is then generated by noting that, for any interaction $-2J_k \hat{S}_i \cdot \hat{S}_j$, the operator only acts on the ith and jth components of the bra and ket so that the matrix element $\langle S_1 S_2 ... S_i ... S_j ... S_N | \hat{S}_i \cdot \hat{S}_j | S'_1 S'_2 ... S'_i ... S'_j ... S'_N \rangle$ factors immediately into $\langle S_1 S_2 ... S_N | S'_1 S'_2 ... S'_N \rangle \langle S_i S_j | \hat{S}_i \cdot \hat{S}_j | S'_i S'_j \rangle$. The first term is either 0 or 1, and the second is a stored number from the matrix of $-2 S_1 \cdot S_2$. The result is multiplied by the particular value of J_k corresponding to that interaction. By cycling through all possible interactions with any number of different values for J_k, the complete matrix can be generated quickly and easily. The magnetic moment matrix can be generated in a very similar way by using $g\beta H S_z$ as the operator. Only two values have to be stored, $+\frac{1}{2}$ and $-\frac{1}{2}$, corresponding to the two possible values of S_z. All the matrix elements are diagonal so it is easy to pick out and sum the N values for each of the 2^N diagonal elements and multiply them by $g\beta H$. [We assume that the interaction is isotropic, and so any anisotropy in the susceptibility arises from the anisotropy in g. Further, because we are fitting average powder susceptibility data, we can use an average g value, and so we can use the $g\beta H S_z$ operator to generate the interaction with the magnetic field. Although we have not done so yet, the method allows a more general analysis involving anisotropy in the exchange interaction (i.e., $J_x = J_y \neq J_z$), in the susceptibility in the x or z direction, and effective field corrections for neighboring spins.] The two matrices are then used as a subroutine for the generalized susceptibility programs VVLH and VVLE.[10] For the present situation, VVLH and VVLE have been modified and streamlined to take account of the extremely large matrices involved, e.g., 252 × 252 for the eight-copper case.

In the present problem the two-dimensional network of $S = \frac{1}{2}$ spin centers can be reduced to an array of M chains, each of which is N copper atoms long (Figure 3). There are two types of exchange pathways, an intrachain-exchange interaction J_1 and an interchain-exchange interaction J_2. The Hamiltonian which describes the Heisenberg spin interactions in this array is shown in eq 2. $f(k,l) = 2l - [1 - (-1)^k]/2$

$$\mathcal{H} = -2J_1 \sum_{i=1}^{M} \sum_{j=1}^{N-1} \hat{S}_{i,j} \cdot \hat{S}_{i,j+1} - 2J_2 \sum_{k=1}^{M-1} \sum_{l=1}^{N'} \hat{S}_{k,f(k,l)} \cdot \hat{S}_{k+1,f(k,l)} \quad (2)$$

and $N' = N/2 - (-1)^k[1 - (-1)^N]/4$. (We wish to thank a reviewer for these more concise expressions than those that were originally in this paper.) $f(k,l)$ is a function which is equal to $2l$ if k is even and $2l - 1$ for odd k, and N' is a function which terminates the interchain interactions at the proper place for all values of M and N. For infinite values of M and N this Hamiltonian represents exactly the interactions in Cu-$(NH_3)_2CO_3$. Obviously, the largest cluster size chosen for the calculations will give the most meaningful results. Unfortu-

(9) *For example, see:* Hall, J. W. Dissertation, The University of North Carolina at Chapel Hill, 1977.

(10) Gregson, A. K. *Aust. J. Chem.*, in press.

Table I. Exchange-Coupling Parameters for Cu(NH$_3$)$_2$CO$_3$

array	J_1,[a] cm^{-1}	J_2,[a] cm^{-1}	Θ, K	R,[b] %
1	-2.2	-3.7		25
2	-12.8	-33		24
3	-5.2	-2.6		4.4
av of 1-3	-5.7	-4.7		14
3	-6.3	-2.3	2.05	2.5
4	-5.3	-3.1		4.5
4[c]	2.52	2.34		
4[c]	1.0	-2.0	1.5	
dimer	-4.4		-2.26	5.1

[a] J_1 and J_2 are designated in the text; see arrays 1-4. [b] Defined by $R = (\Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma(\chi_{obsd})^2)^{1/2}$; % R = 100R. [c] Reference 7.

nately, the largest cluster size which retains the structural features of the extended lattice for which we could conveniently carry out a least-squares refinement of the data with VVLE was six. There are three different sets of interactions between six copper atoms in the array shown in Figure 3. These interaction pathways are schematically represented as 1-3, where the numbering of the copper ions is that set out in Figure 3.
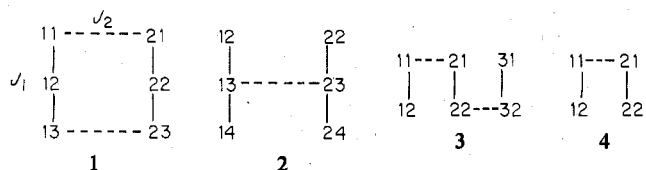
We tried first to fit the experimental susceptibility data to each of the interaction arrays (1-3) and then to the average of them, the reasoning for the calculation of an average being that if each array was a reasonable approximation to the infinite case, an average of the three might be an even better representation. The results of the calculations are shown in Table I [all calculations were done with the experimental g value (2.18)[11] and the experimental applied magnetic field (1 T)[6]] and Figure 4, where it is clear that array 3 gives the best fit to the experimental data. This array is similar to the first six copper atoms of an alternating Heisenberg chain for which the susceptibility has been derived from an extrapolation of a ten-spin-$^1/_2$ cluster model.[12] This has been programmed in our laboratory,[9] and the fit is nearly identical with that represented by array 3. Any differences are obviously absorbed into the slightly different values for the exchange constants which were obtained, those being J_1 = -5.06 cm^{-1} and J_2 = -2.04 cm^{-1}. We also tried one further modification to the alternating chain represented by array 3. If we assume that all the other interactions are represented by a correction term Θ as in $\chi = \chi/(1 - \Theta/T)$, then an improved fit is obtained, but the parameters are probably of doubtful significance.

The four-spin cluster (array 4) also gives a fair fit to the experimental susceptibility data (Table I and Figure 5). This is the simplest form of an alternating Heisenberg chain, and, statistically, the fit is nearly as good as that obtained for array 3, with the differences in the models being absorbed into the different parameter values. The parameters of Kamase et al.[7] have also been included and are plotted in Figure 5. As expected, they show no maximum in the susceptibility. As explained above, Kamase et al.[7] have compared their model with calculated magnetization data rather than the experimental susceptibility data. We have confirmed this by reproducing the calculated magnetization curve with use of their models and their parameters.

The values for the two exchange-coupling constants are interesting for several reasons. The intrachain interaction of

-5.2 cm^{-1} is antiferromagnetic in nature. As far as is known there are only three other well-characterized copper compounds where the carbonate ion acts as a bridging ligand to form an extended lattice. These are the chainlike Na$_2$Cu(CO$_3$)$_2$·3H$_2$O,[13] the two-dimensional layered structure of Na$_2$Cu(CO$_3$)$_2$,[14] and the three-dimensional K$_2$Cu(CO$_3$)$_2$.[15] In each of these three materials the carbonate ion functions as a bridging ligand with one oxygen from a given carbonate coordinated to one copper, the second oxygen coordinated to a second copper atom thus propagating the lattice, while the third oxygen remains uncoordinated. In Na$_2$Cu(CO$_3$)$_2$·3H$_2$O there is also a bidentate carbonate group which plays no part in the formation of the chain structure. The magnetic interaction in each of these compounds is ferromagnetic in nature: in Na$_2$Cu(CO$_3$)$_2$·3H$_2$O, J = ~1 cm^{-1};[16] in Na$_2$Cu(CO$_3$)$_2$, the intralayer coupling is +4.1 cm^{-1}; [17,18] in the three-dimensional K$_2$Cu(CO$_3$)$_2$, J = 1.2 cm^{-1}.[18] The bridging carbonate group in Cu(NH$_3$)$_2$Co$_3$ is bidentate; it is the third oxygen which coordinates to the neighboring copper to propagate the lattice. This quite different bridging geometry must bring about the antiferromagnetic interaction. The interchain interaction is also interesting because it appears to be one of the few cases where a through-space interaction can be documented. One example is in α-bis(N-methylsalicylaldiminato)copper(II) where the planar molecules stack up to form a chain with a direct through-space intrachain separation of 3.3 Å.[19] The direct interaction in this compound is antiferromagnetic in nature with an exchange-coupling constant of -2.2 cm^{-1}.[20] This is quite similar to the present Cu(NH$_3$)$_2$CO$_3$ where the direct copper-copper interchain distance is 3.5 Å and the coupling constant is -2.6 cm^{-1}; however, we must point out the hydrogen-bonding network in Cu(NH$_3$)$_2$CO$_3$ may provide a pathway for superexchange interactions.

Conclusion

The cluster approach to the problem of exchange interactions in the two-dimensional layer compound Cu(NH$_3$)$_2$CO$_3$ has been reasonably successful in accounting for the experimental susceptibility data of the compound. The structure of this material is complicated, and, consequently series-expansion and high-symmetry models are not of much use because of the nature of the interactions present. Using the cluster approach, we have defined exactly the different interactions, but unfortunately we were limited to the number of atoms than could be considered explicitly in the present program with available computational facilities. A six-copper cluster which is comparable to the alternating Heisenberg chain gives as good agreement as that based on an extrapolation of the ten-atom case. However, it must be appreciated that, when clusters are considered as a representation for extended arrays, smaller clusters with the correct type of interaction(s) may fit the experimental data fairly well, with the differences between the small clusters and the larger more realistic clusters being absorbed into the different parameter

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(14) (a) Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1913. (b) White, A. H., private communiction.
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values. In this regard the modified dimer model of Jeter et al.[6] gives nearly as good a representation of the experimental data as the larger cluster size models. However, on the basis of the structural data, we conclude that this is not a good physical picture of the material.

Contribution from the Department of Physical Chemistry,
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Solubility and Equilibrium Constants of Mercury(II) in Carbonate Solutions (25 °C, I = 0.5 mol dm⁻³)[1a]

HALKA BILINSKI,*[1b] MILENKO MARKOVIĆ, and MARIJAN GESSNER

Precipitation and dissolution studies of mercury(II) in carbonate solutions, performed at $I = 0.5$ mol dm⁻³ and 25 °C, complete the present knowledge of the state of inorganic divalent mercury in natural waters. The turbidity method was used to detect precipitation regions. Chemical analysis, IR spectra, and X-ray diffraction patterns were used to distinguish the various Hg salts in different concentration regions. The concentrations of mercury and hydrogen ions have been determined in solution in contact with the solid phase. From experimental data the following values for equilibrium constants are obtained: log $[Hg^{2+}]^3 p(CO_2)[H^+]^{-6} = 5.40$; log $[HgOH^+][H^+][Hg^{2+}]^{-1} = -3.38$; log $[Hg(OH)_2^0][H^+]^2[HgOH^+] = -2.56$; log $[HgHCO_3^+][Hg^{2+}]^{-1}[CO_3^{2-}]^{-1} = 15.08$; log $[HgCO_3^0][Hg^{2+}]^{-1}[CO_3^{2-}]^{-1} = 11.01$; log $[HgOHCO_3^-][H^+][Hg^{2+}]^{-1}[CO_3^{2-}]^{-1} = 4.40$; log $[Hg(CO_3)_2^{2-}][Hg^{2+}]^{-1}[CO_3^{2-}]^{-2} = 14.50$.

Introduction

There is limited information about the mercury(II) carbonate system in the literature, although it might be of interest in geochemistry. Several basic salts have been prepared.[2] The solubility product of $HgCO_3 \cdot 2HgO(s)$ has been determined at $I = 3.0$ mol dm⁻³, independently by Hietanen and Högfeldt[3] and by Weber.[4] Soluble complexes were studied by Hietanen and Högfeldt.[5] They have calculated equilibrium constants for the three soluble mercury carbonate species $HgHCO_3^+$, $HgCO_3^0$, and $HgOHCO_3^-$. According to them the formation of $HgCO_3^0$ is somewhat uncertain considering the experimental uncertainty. In this work there is shown the concentration range of three stable solids, formed in mercury(II) carbonate system. Solubility of $HgCO_3 \cdot 2HgO(s)$ and equilibrium constants of soluble complexes are determined at $I = 0.5$ mol dm⁻³. The values at $I = 3.0$ mol dm⁻³ obtained by Hietanen and Högfeldt[5] are recalculated and discussed.

Experimental Section

Chemicals. Solutions were prepared by dissolving the following chemicals in bidistilled water: $Hg(NO_3)_2$, $HClO_4$, $NaClO_4 \cdot H_2O$, $NaHCO_3$, NH_4OH (Merck, Darmstadt, Germany), pa; Na_2CO_3, EDTA, Zn metal powder (Kemika, Zagreb, Yugoslavia). Indicator buffer (Merck) was used for mercury determination. Stock solutions were standardized.

Solubility experiments were performed in two ways. (a) Prepared solid $HgCO_3 \cdot 2HgO$ was equilibrated with solutions of the composition

Table I. X-ray Powder Pattern[a] for HgCO₃·2HgO

d_{obsd}, Å	I	d_{obsd}, Å	I
5.63	18	2.12	8
5.50	27	2.099	30
3.62	6	2.070	6
3.23	8	1.821	27
3.15	35	1.734	10
3.03	41	1.667	4
2.82	52	1.639	4
2.75	100	1.613	28
2.41	10	1.581	9
2.38	7	1.530	20
2.22	6	1.524	21
2.19	8	1.514	22

[a] The instrument used was a Philips PW 1050 X-ray diffractometer (Cu Kα radiation).

$[H^+] = H$ mol dm⁻³, $[Na^+] = (0.5 - H)$ mol dm⁻³, $[ClO_4^-] = 0.5$ mol dm⁻³, and $CO_2(g)$. In calculation of $p(CO_2)$, the partial pressure of water vapor of 23.75 torr was used. The dissolution time was 1–2 days. The reaction vessel and emf cell were the same as those described by Schindler, Reinert, and Gamsjäger.[6] In each equilibrated solution the concentrations of soluble mercury and free hydrogen ions were determined. (b) Solid $HgCO_3 \cdot 2HgO$ was precipitated by mixing a solution of mercury nitrate with a carbonate solution of the composition $[HCO_3^- + CO_3^{2-}]$ mol dm⁻³, $[Na^+] = 0.5$ mol dm⁻³, and $[ClO_4^-] = (0.5 - [HCO_3^- + 2CO_3^{2-}])$ mol dm⁻³. Thirty days was allowed for equilibrium.

Instruments. The presence or absence of solid phases detected tyndallometrically[7] (a Zeiss tyndallometer in combination with a Pulfrich photometer) and color with the naked eye. X-ray diffraction patterns and IR spectra were used to distinguish the various Hg salts in different concentration regions. The concentration of soluble mercury was determined either by rapid DC polarography method[8] using Metrohm Polarecord E 261 or by a complexometric method.[9]

(1) (a) This work has been presented in part at the Congress sur la protection des eaux de mer, lacs, et rivieres, Belgrade, Yugoslavia, Oct 26–30, 1976, and in part at the Conference on Electrolyte Precipitation in Aqueous Solution, Copenhagen, Denmark, Aug 16–18, 1978. (b) Dc polarographic measurements have been performed by H.B. at EAWAG, ETH-Dübendorf, Switzerland.
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