oxygen atom transfer may then occur via either a nitrito (Scheme II) or a nitro isomer (Scheme I). The oxygen atom transfer step would appear to be facilitated by the larger ring formed by a nitrito ligand in the transition state in Scheme II, while thermodynamics would favor the direct formation of the N-bonded isomer of the nitrosyl ligand in Scheme I. At the present time, there is insufficient experimental evidence available to distinguish between these two possible reaction routes. In spite of the uncertainty regarding which of the two NO_2 linkage isomers is responsible for the oxygen atom transfer to CO, it is clear that the reaction proceeds via the formation of a five-coordinate carbonyl intermediate. Moreover, once the oxygen atom is transferred from the NO_2 ligand to the CO ligand, CO_2 is lost *before* it can exchange with the resulting NO and NO_2 ligands. CO_2 and $Ni(NO_2)(NO)L_2$ are produced quantitatively, but at rates that are dependent upon L. Our studies also show that *^{18}O is not incorporated into the nickel products*, even though some scrambling of the ^{18}O and ^{16}O isotopes in CO_2 was observed.

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Registry No. $Ni(NO_2)_2(PMe_3)_2$, 20663-81-4; $Ni(NO_2)_2(PEt_3)_2$, 86941-01-7; $Ni(NO_2)_2(PMe_2Ph)_2$, 25456-46-6; $Ni(NO_2)_2(PMePh_2)_2$, 86886-05-7; $Ni(NO_2)_2(PCy_3)_2$, 86886-06-8; $Ni(NO_2)_2(P\text{-}n\text{-}Bu_3)_2$, 24510-66-5; $Ni(NO_2)_2$dppe, 71604-08-5; $Ni(NO_2)_2$(*cis*-vpp), 86886-07-9; $Ni(NO_2)_2$dppp, 86886-08-0; $Ni(NO_2)(NO)(PMe_3)_2$, 79499-32-4; $Ni(NO_2)(NO)(PEt_3)_2$, 86886-09-1; $Ni(NO_2)(NO)(PMe_2Ph)_2$, 86886-10-4; $Ni(NO_2)(NO)$dppe, 86886-11-5; $Ni(NO_2)(NO)$(*cis*-vpp), 86886-12-6; $Ni(NO_2)(NO)$dppp, 86886-13-7; $Ni(NO_2)(NO)(PCy_3)_2$, 86886-14-8; CO, 630-08-0.

Contribution from the Department of Chemistry,
Carleton College, Northfield, Minnesota 55057

Copper(II) Chloride Complex Equilibrium Constants

RICHARD W. RAMETTE* and GRACE FAN

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The solubility of recrystallized copper iodate hydrate was determined, by using high-accuracy controlled-potential coulometry, in solutions of copper perchlorate and in solutions of sodium chloride, all at ionic strength 5 with sodium perchlorate as the inert electrolyte. The association constant for the $CuIO_3^+$ species and the solubility product for copper iodate were determined at 25 and 35 °C. From the effects of chloride ion on the solubility at 25 °C, the four successive β values for copper chloride complexes were determined and compared with results of spectrophotometric measurements. Revised enthalpy changes for the complexation steps were calculated.

The thermodynamic characterization of the reactions that occur when chloride ion is added to a copper(II) perchlorate solution is an inorganic chemistry problem of long standing. The color changes gradually from blue to green with increased absorption both in the ultraviolet (250–275 nm) and at the high end of the visible spectrum (700–800 nm). Absorption spectra of the solutions have been repeatedly examined with the goal of determining the equilibrium constants for the formation of the successive complexes

$$M + jL = ML_j$$

where j = 1–4 and M and L represent the tetraaquocopper(II) ion and the chloride ion, respectively. The system may be described in terms of β values, which are overall equilibrium constants $\beta_j = [ML_j]/[M][L]^j$, or in terms of the individual equilibrium constants for each step $Q_j = [ML_j]/[ML_{j-1}][L]$.

A recent paper by Arnek et al.[1] presents a calorimetric study of the system and includes a useful summary of previous equilibrium research under a variety of conditions of ionic strength.

Three studies of this system have been reported for an ionic strength of 5, permitting the high chloride concentrations needed for appreciable formation of the higher complexes. Schwing-Weill[2,3] obtained a comprehensive set of ultraviolet–visible spectra for a large number of copper–chloride mixtures and applied least-squares analysis to estimate values for the equilibrium constants and for the molar absorptivities. Bjerrum and Skibsted[4] suggested reinterpretation of Schwing-Weill's data on the basis of data in very concentrated chloride media. Ashurst and Hancock[5] used their own data under selected conditions to obtain another set of equilibrium constants. The lack of agreement in these studies gives support to the closing paragraph of Bjerrum and Skibsted:

"The conclusion of this paper is that attempts to obtain quantitative results in studies of consecutive weak complex formation in solution necessitate the use of many approximations, and studies of such systems can therefore be expected to give only semiquantitative results."

Given the inherent problem of the spectrophotometric approach to this system, namely that the data must be treated with both the equilibrium constants and the molar absorptivities as unknown parameters, it seemed very desirable to study the copper–chloride system by using a method completely independent of spectrophotometry, i.e. by measuring the effect of varying chloride concentration on the solubility of copper(II) iodate. Accurate equilibrium constants are also required for the interpretation of the calorimetric study,[1] which also was performed at ionic strength 5.

The theoretical and computational basis for the use of solubility of a metal iodate as a chemical probe for finding metal–ligand complex formation constants has been described for an analogous study of cadmium bromide complexes.[6] The

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(1) Arnek, R.; Puigdomenech, I.; Valiente, M. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 15–9.

(2) Schwing-Weill, M. J. *Bull. Soc. Chim. Fr.* **1973**, 823–30.

(3) Khan, M. A.; Schwing-Weill, M. J. *Inorg. Chem.* **1976**, *15*, 2202–5.

(4) Bjerrum, J.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 673–7.

(5) Ashurst, K. G.; Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1981**, 245–50.

0020-1669/83/1322-3323$01.50/0

present work is concerned with the effect of varying sodium chloride concentration on the solubility, S, of copper iodate. The key relationships are

$$MA_2(s) = M + 2A \qquad K_{sp} = [M][A]^2 \qquad (1)$$

$$M + A = MA \qquad K_1 = [MA]/[M][A] \qquad (2)$$

$$S - [MA] = C_M = [M] + [ML] + [ML_2] + [ML_3] + [ML_4] \qquad (3)$$

where A represents the iodate ion and ionic charges are omitted for simplicity. The solubility was determined by controlled-potential coulometry, using reduction of dissolved iodate at a platinum cathode. The data were corrected for the slight formation of the MA ion pair to give values for C_M. The concentration of the uncomplexed copper(II) ion was calculated from the iodate ion concentration by using the solubility product for copper iodate. The formation function, $F_0 = C_M/[M]$, follows. The F_0 values are related to the equilibrium constants and to the equilibrium concentration of chloride:

$$F_0 = 1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4 \qquad (4)$$

An iterative least-squares procedure that includes correction of the total sodium chloride concentration, C_L, for the chloride used in forming the complexes yields the set of β values that best describe the data.

Experimental Section

Copper iodate was prepared by slow addition of sodium iodate and copper sulfate solutions simultaneously to rapidly stirred hot 0.1 M nitric acid. The thoroughly washed precipitate was placed in a Soxhlet extractor, using a fritted-glass crucible in place of the usual thimble, and with 0.02 M nitric acid in the boiling flask, a recrystallized product was obtained over a period of 1 week. The copper iodate thus obtained consisted of clear, greenish blue crystals in contrast to the opaque clumps of microcrystals formed by direct precipitation. When samples of this product were heated to constant weight at 300 °C, the mass loss was precisely in accord with the formula $3Cu(IO_3)_2 \cdot 2H_2O$, in agreement with the findings of Nassau et al.,[7] who examined a variety of preparations and concluded that copper iodate formed from nitric acid solutions was identical in composition with the mineral bellingerite.

The preparation and sampling of saturated solutions of copper iodate were accomplished by the techniques described[8] for a study of cadmium iodate solubility. However, the coulometry cell solution also contained 0.02 M EDTA to mask the copper(II) against reduction either by the iodide ion or by the cathode. This was important to eliminate any interference by dissolved oxygen, which would reoxidize Cu(I), and made it unnecessary to deaerate the solutions.

All solutions were prepared and analyzed on a mass basis to eliminate volumetric errors. Later conversion of data to a molarity basis required determination of solution densities by weighing precise volumes delivered by a standardized and siliconized pipet. Density data were used in smoothed form after a least-squares fit. All solutions had an ionic strength of 5.0 and were prepared with water redistilled from alkaline permanganate. Copper perchlorate stock solutions were standardized by visual EDTA titration using murexide, by potentiometric EDTA titration using a mercury electrode, and by controlled-potential coulometric deposition and stripping using both mercury-pool and platinum-gauze cathodes. The accuracy and precision of the coulometric determination of iodate were checked with solutions of recrystallized potassium iodate, with standard deviations of about 0.03%. All solutions were prepared with reagent grade sodium chloride, with use of sodium perchlorate to adjust the ionic strength to 5.00.

Experience showed that the solid phases of copper iodate were slow in reaching their final values of solubility. Fresh portions of solutions were added repeatedly until the observed solubilities were reproducible to an uncertainty of less than 1 ppt. After results were obtained at 25 °C, the solubilities were determined at 35 °C.

Table I. Solubility and Thermodynamic Quantities for Copper Iodate in Copper Perchlorate

	25 °C		35 °C	
C_L mol/L	S_{obsd}, mmol/L	S_{calcd}, mmol/L	S_{obsd}, mmol/L	S_{calcd}, mmol/L
0.010 392	2.011	2.016	2.085	2.090
0.021 091	1.530	1.524	1.590	1.584
0.031 631	1.291	1.290	1.344	1.343
0.042 115	1.146	1.149	1.195	1.198
0.052 801	1.053	1.052	1.098	1.098
K_{sp}	$1.893\ (0.009) \times 10^{-7}$		$2.034\ (0.009) \times 10^{-7}$	
K_1	2.23 (0.07)		2.35 (0.07)	

	ΔG, J/mol	ΔH, J/mol	ΔS, J/(mol K)
reaction 1	+38370	+5484	−110
reaction 2	−1992	+3906	+19.8

Table II. Solubility of Copper Iodate and Overall Equilibrium Constants for Copper Chloride Complexes in Sodium Chloride Solutions at 25 °C

C_L, mol/L	$[Cl^-]_{equil}$, mmol/L	S_{obsd}, mmol/L	S_{calcd}, mmol/L	F_0
0.099 00	0.098 16	3.944	3.939	1.261
0.199 60	0.197 97	4.219	4.216	1.549
0.298 07	0.295 67	4.477	4.480	1.856
0.401 41	0.398 19	4.739	4.756	2.206
0.502 33	0.498 27	5.003	5.026	2.602
0.698 75	0.692 98	5.555	5.559	3.573
0.798 63	0.791 94	5.864	5.835	4.209
1.296 4	1.284 8	7.302	7.270	8.163
1.696 7	1.680 8	8.513	8.492	12.96
2.496 7	2.471 8	11.06	11.07	28.46
3.503 2	3.466 6	14.40	14.49	62.94
4.990 4	4.936 0	19.86	19.78	165.2

β values: 2.49 (0.09), 1.14 (0.21), 0.90 (0.13), 0.025 (0.020)

Table III. Solubility of Copper Iodate and Overall Equilibrium Constants for Copper Chloride Complexes in Sodium Chloride Solutions at 35 °C

C_L, mol/L	$[Cl^-]_{equil}$, mmol/L	S_{obsd}, mmol/L	S_{calcd}, mmol/L	F_0
0.098 70	0.097 76	4.060	4.062	1.278
0.198 99	0.197 11	4.384	4.377	1.616
0.297 17	0.294 37	4.694	4.685	1.990
0.400 20	0.396 41	5.001	5.008	2.412
0.500 80	0.496 03	5.305	5.325	2.886
0.696 62	0.689 87	5.936	5.951	4.057
0.796 19	0.788 40	6.290	6.273	4.836
1.292 4	1.279 1	7.952	7.929	9.814
1.691 5	1.673 5	9.337	9.320	15.92
2.488 9	2.460 7	12.21	12.24	35.71
3.492 1	3.450 0	16.13	16.15	82.37
4.974 2	4.909 7	22.35	22.32	219.3

β values: 2.66 (0.09), 1.99 (0.21), 0.88 (0.13), 0.091 (0.020)

Results

The solubility of copper iodate was determined in five solutions of copper perchlorate, and the results are shown in Table I. The data were interpreted with the program KSPK1FIT. The uncertainties were obtained by simulating the experiment 10 times with the program GENKSPK1, which generated data with the imposition of a specified standard deviation of 2 ppt in the solubility measurements.

The solubility of copper iodate was determined in 12 solutions of sodium chloride ranging from 0.1 to 5 mol/L. The slight increase in solution volume due to the dissolving of the solid was calculated by assuming that the molar volume of aqueous copper iodate is the same as that of the pure solid.

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(6) Ramette, R. W. *Anal. Chem.* **1983**, *55*, 1232–6.

(7) Nassau, K.; Shiever, J. W.; Prescott, B. E. *J. Solid State Chem.* **1973**, *7*, 186–204.

(8) Ramette, R. W. *Anal. Chem.* **1981**, *53*, 2244–6.

Table IV. Equilibrium Constants and Thermodynamic Quantities

	complex			
	ML	ML_2	ML_3	ML_4
a	4.0 (0.7)	4.7 (0.6)	2.0 (0.3)	0.23 (0.05)
b	2.49 (0.09)	1.14 (0.21)	0.90 (0.13)	0.025 (0.020)
c	−2.26 (0.09)	−0.32 (0.42)	0.26 (0.33)	9.1 (1.6)
d	12.3 (0.1)	23.0 (1.5)	11 (4)	
e	9.0 (0.1)	15.5 (1.7)	19.8 (0.9)	
f	37.7 (0.5)	53 (5)	66 (3)	

[a] β values from ref 3. [b] β values from present work. [c] Gibbs free energy change (kJ/mol) from β values of present work. [d] Enthalpy change (kJ/mol) from ref 1 with β values from ref 4. [e] Revised enthalpy change (kJ/mol) from β values of present work with calorimetric data from ref 1. [f] Entropy changes (J/(mol K)) corresponding to lines *c* and *e*.

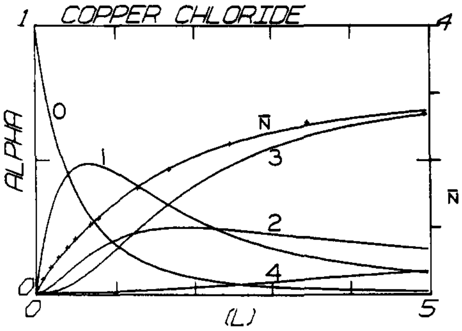

Figure 1. Distribution (fraction) of $CuCl_j^{2-j}$ as a function of chloride concentration. The + marks are the experimental values of $\bar{n}$, the average ligand number. The smooth curve through the points was calculated by using the β values determined in the present work. Curves were plotted by the program BETAPLOT.

The data and calculated β values are given in Tables II and III. The calculated solubilities were found by using the previously determined K_{sp} and K_1 values, together with the β values, in the program GENSOLDAT. The standard deviation in the solubility values is about 4 ppt, which corresponds to 8 ppt in the F_0 values. This uncertainty is due to slight differences in behavior of the 12 solid phases in the equilibrium system, not to errors of equilibration, sampling, or coulometric analysis. For comparison, these uncertainties are equivalent to a hypothetical potentiometric study, using a copper ion electrode, with a standard deviation of only 0.1 mV in the measurement of cell potential. To obtain an estimate of the uncertainties in the derived β values, the experiment was simulated 10 times with the program GENSOLDAT, with the specification of 4 ppt standard deviation in the solubility data. Random errors were imposed on the data by a subroutine that provides a Gaussian distribution. The simulated data were treated by the same calculation procedures, using the programs FIXSOLDAT (to correct for the MA ion pair) and FORMSOLVE, and 10 sets of β values resulted. The standard deviations are shown in parentheses in the tables.

Table IV shows the β values from this and the earlier works. Figure 1 is the conventional type of distribution diagram and includes the values of the average ligand number $\bar{n}$ calculated from the data, $\bar{n} = (C_L - [L])/C_M$, along with the smooth curve for $\bar{n}$ calculated from the β values.

Discussion

The values of K_{sp} and K_1 were accurately determined at two temperatures. Although the temperature range was only 10 °C, it seems valid to calculate the thermodynamic quantities shown in Table I. There are no other literature data on the values of K_{sp} and K_1 at ionic strength 5 and no previous determinations of K_1 under any conditions.

From the distribution diagrams it is clear that, even when the chloride concentration is 5 mol/L, only a small fraction of the copper is converted to the ML_4 complex. This makes the value of β_4 much less reliable than the other values. However, when the data are treated on the assumption that only three complexes are formed, the least-squares fit is less satisfactory.

For reasons presented below, we consider the detailed work by Schwing-Weill to be the only other experimental study capable of determining the set of four equilibrium constants. She used 37 copper solutions ranging from 0.005 to 5 mol/L in chloride concentration and determined absorbances at 12 different wavelengths. An iterative least-squares algorithm treated the 324 data points in terms of 52 adjustable parameters (48 molar absorptivities and 4 equilibrium constants) to obtain the best fit to the data. The success of this approach is strongly dependent upon the accuracy of the raw data, as we have found by computer simulations (program GENSPEDAT) that included a specified standard deviation in absorbance measurements. In the presence of normal spectrophotometric error, imposed randomly on a number of different simulations, the data yield a wide range of equilibrium constants, with sets of diverse values serving equally well to fit the data. This is because the programs must simultaneously optimize both the equilibrium constants and the absorptivities, and errors in the constants may be essentially offset by errors in the absorptivities. This problem is especially severe for the determination of β_4.

The contribution by Bjerrum and Skibsted presents a very different set of β values based largely on speculation rather than experiment and cannot be considered a valid revision of Schwing-Weill's results. The list of assumptions deserves comment. They assumed that the copper was nearly completely converted to the ML_4 complex in 6.2 M calcium chloride solution. But, leaving aside the possibility of a severe medium effect in this solution as compared to 5 M sodium chloride, Bjerrum and Skibsted's own proposed value for Q_4 would lead to the prediction that about 50% of the copper would still be in the form of the ML_3 complex. They assumed that only the ML_4 complex will absorb light at 436 nm, but there is no direct experimental evidence for this. They also assumed that the molar absorptivity of this complex would be the same in Schwing-Weill's solutions as it appeared to be in the 6.2 M calcium chloride, an unlikely event. They assumed that the equilibrium constants would be interrelated in accord with a statistically calculated ligand effect, which is interesting but not a valid substitute for experiment. They then picked a set of equilibrium constants consistent with the foregoing assumptions and with the data and assumptions for the calcium chloride solutions.

Finally, the experimental study by Ashurst and Hancock must be discussed. First, these authors attempted to find a value for Q_1 by measuring the absorbance of six solutions containing 0.03 mol/L chloride and varying concentrations of copper(II) up to 0.1 mol/L. A computer program, SPEFO, was used to calculate a value of $Q_1 = 1.43$ on the valid assumption that negligible amounts of the ML_2 complex would be present. However, an examination of the data shows that this attempt to determine Q_1 is not successful.

The data, based on the assumption that only one complex is present, must be in accord with the equation[9]

$$Q_1 = E/[L](E_1 - E) \qquad (5)$$

where E is the apparent absorptivity of the copper–chloride solution, E_1 is the unknown molar absorptivity of ML, and [L] is the equilibrium molarity of chloride. When the data (from Figure 1 of the Ashurst and Hancock paper[5]) are examined in light of this equation, it is clear that they are ill-conditioned.

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(9) Ramette, R. W. *J. Chem. Educ.* **1967**, *44*, 647–54.

The problem is that in the six solutions the equilibrium chloride concentration does not vary significantly. In effect, the six data values are virtually equivalent to a single data point and, even with very slight errors in E, it is impossible to find reasonable values for both unknowns, Q_1 and E_1. We have made an estimate of the value for E_1 by using the equilibrium constants from the present work with Schwing-Weill's absorbance data at 250 nm (the wavelength used by Ashurst and Hancock[5]). We find using program PHOSOLVE that the molar absorptivity of the ML complex is 1770. If this value of E_1 is assumed to hold for the Ashurst–Hancock experiment, we calculate a value of 2.3 for Q_1 from their data. This is close to our value of 2.5 from the solubility data. The other equilibrium constants deduced by Ashurst and Hancock are dependent upon the value for Q_1 and are subject to additional assumptions.

We turn now to the calorimetric study,[1] which used a flow microcalorimeter and chloride concentrations ranging up to about 3 mol/L. Given the small value of Q_4, these data will not yield information about the ML_4 step in the complex system but are adequate for finding enthalpy changes for the first three steps. Interpretation of the data requires a set of equilibrium constants from other experiments, and these authors adopted the values proposed by Bjerrum and Skibsted. We have reinterpreted the calorimetric data using the equilibrium constants from the present work to obtain values for the enthalpy and entropy changes, using program CALSOLVE. The results are given in Table IV. It is encouraging that the enthalpy changes calculated with the β values from the present work show a trend, rather than the sharp change of direction (Table IV, line d) found for the ML_3 complex when the β values of Bjerrum and Skibsted are used with Arnek's data. Further, the present β values give a somewhat better fit to the calorimetric data, as has been verified by Professor Arnek.[10]

In conclusion, the solubility approach has yielded equilibrium constants that are independent of spectrophotometric measurements. Future work will be aimed at improving the consistency of the solubility behavior of metal iodates because, given the present techniques of sampling and coulometric determination, it should be possible to reduce the standard deviation of the solubility determinations by a factor of 10. Such an improvement would greatly decrease the uncertainty in the derived equilibrium constants.

It is possible that the spectrophotometric study and the solubility study will necessarily yield different sets of β values and that neither set is "correct". The true equilibrium constants for the system are those defined in terms of activities of the species, even if we adopt the 5 M sodium perchlorate solution as the reference state for ideal behavior. In both methods the aqueous medium has been varied from 5 M perchlorate to 5 M chloride, and it is highly unlikely that our assumption of constant activity coefficients is valid. However, that doubt applies to both methods. The special problem in the solubility method is our need to assume that the activity coefficients of iodate ion and the copper–iodate ion pair remain constant. We make this assumption implicitly when we use the values for K_{sp} and K_1 obtained in the perchlorate medium, and we recognize this fundamental limitation in the solubility approach.

The special problem in the spectrophotometric method is the need to assume that the four molar absorptivities of the copper chloride complexes are not affected by the change in medium. This is also improbable, as we have shown by preparing solutions of the copper ethylenediamine complex in 5 M sodium perchlorate and in 5 M sodium chloride. The absorption maxima are at 538 and at 551 nm, respectively, and the molar absorptivity is about 15% higher in the chloride medium. If the molar absorptivities of the copper chloride complexes are also subject to such variation, then there is little hope of determining the "true" β values by spectrophotometric studies.

Similar questions arise when we consider the classical potentiometric method of studying metal complexes and also in calorimetric measurements when the ionic medium must vary widely. How nearly constant are the standard potential and the response slope of the metal electrode? How do the molar enthalpy changes for the complexation steps vary with drastic changes in medium?

The conclusion is that our careful equilibrium and calorimetric studies may be less a determination of fundamental properties than a description of the combined behavior of the complex system and the particular probe that is being used in the study.

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Appendix

The calculations used in this research involve several computer programs, written in DEC VAX-11 Basic, and further information may be obtained from the authors. The program are as follows:

GENKSPK1 generates solubilities of divalent metal iodate in specified solutions of the metal perchlorate, given values of K_{sp} and K_1. The resulting data (or actual experimental data) are interpreted by KSPK1FIT to find the values for K_{sp} and K_1.

GENSOLDAT generates solubilities of metal iodate in specified solutions of complexing ligand, given K_{sp}, K_1, and the β values. The resulting data are first treated by FIXSOLDAT to correct for the metal–iodate ion pair and are then interpreted by FORMSOLVE to find the best set of β values.

GENSPEDAT generates absorbances for solutions of metal ion in specified solutions of complexing ligand L, given the β values and the molar absorptivities for the complexes. The data are interpreted by SPECSOLVE to find the best set of β values and absorptivities. If the β values are known from other experiments, the program PHOSOLVE will use them to find the molar absorptivities from the data.

GENCALDAT generates heat effects for specified mixtures of metal ion and complexing ligand, given the β values and the enthalpy changes. The data are interpreted by CALSOLVE, given a set of β values, to find the best set of enthalpy changes.

Registry No. $Cu(IO_3)_2$, 13454-89-2.

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[10] Arnek, R., private communication.