to the low solubility of cuprous chloride in organic solvents. We have found that the rate of oxidation of a slurry of cuprous chloride in acetic acid containing excess chloride is constant with time to the point where the formation of cupric chloride has appreciably altered the chloride ion concentration. This constancy no doubt results from the rapid dissolution of cuprous chloride maintaining a constant equilibrium concentration of dissolved cuprous copper. Since the concentration of cuprous copper can be varied over a wide range by varying the chloride ion concentration, we have a convenient means of measuring the kinetics of the oxidation of cuprous copper in acetic acid.

Experimental Section

Reagents.—The cuprous chloride, acetic acid, and lithium chloride were of reagent grade. They were used without further purification. The oxygen was Air Reduction Co, U.S.P. grade.

Kinetic Runs.—The majority of runs were made using creased flasks connected to thermostated gas burets. This technique has been described.[4] A 2.45-g portion of the cuprous chloride was mixed with 25 ml of a glacial acetic solution of lithium chloride of a known molarity in the reaction flask. The solution was put under an oxygen atmosphere and the stirrer started. The rate was followed by measuring oxygen uptake. A solution identical with the reaction mixture was agitated under a nitrogen atmosphere for a few minutes and the supernatant analyzed for Cu(I). The Cu(I) was determined by difference between Cu(II) and total copper. The Cu(II) was first determined by adding KI to an aliquot of the supernatant and titrating the I_2 released with standard thiosulfate. Another portion was evaporated to dryness, all the copper oxidized to Cu(II) with nitric acid, and the Cu(II) then determined in the same fashion.

Two of the runs, one at 1 atm and one at 3 atm, were made in a modified Sutherland reactor.[5] The pressure was maintained by means of a large mercury manometer equipped with thermowatch controller. Gas from a thermostated reservoir was fed automatically following a pressure drop of 1 mm. The reaction was followed by the pressure drop of the thermostated reservoir.

Results

The plot of oxygen uptake *vs.* time was linear until the chloride concentration was changed appreciably by the oxidation of cuprous chloride to cupric chloride. The time during which a constant rate was observed varied with the original [Cl$^-$] but, in general, the curvature was detectable when the moles of Cu(I) oxidized was equal to 5% of the moles of total soluble chloride originally present. Results are given in Table I.

The value of k_3 in the last column of Table I is calculated from the relationship

$$-\frac{d[\mathrm{Cu(I)}]}{dt} = k_3[\mathrm{Cu(I)}]^2[P_{\mathrm{O}_2}] \qquad (1)$$

The soluble Cu(I) is probably present as $LiCuCl_2$ since $CuCl_2$ is the predominant species of soluble Cu(I) in aqueous chloride solutions[6] and this is the most likely form in acetic acid containing chloride.

Discussion

Although the variation in k_3 is almost a factor of 2, the range of rates measured was a factor of over 1000, so there is little doubt that eq 1 is the correct kinetic expression.

TABLE I

RATE DATA FOR THE OXIDATION OF CUPROUS CHLORIDE IN ACETIC ACID AND AT 25° AND VARIOUS CHLORIDE ION CONCENTRATIONS

[LiCl], M	[Cu(I)], M	[H$^+$],[a] M	Oxygen pressure, atm	Rate, M sec^{-1} × 10^6	k_3 × 10^3, M^{-1} atm^{-1} sec^{-1}
0.1	0.0118	...	1	0.58	4.2
0.25	0.044	...	1	8.9	4.6
0.5	0.090	...	1	64.5	8.0
1.0[b]	0.211	...	1	283.0	6.3
1.0	0.211	...	1	220.0	4.9
1.0[b]	0.211	...	3	880.0	6.6
2.0	0.299	...	1	655.0	7.3
1.0	0.211	0.1	1	230.5	5.2
1.0	0.211	0.2	1	231.0	5.2
1.0	0.211	0.5	1	202.0	4.5

[a] Added as CH_3SO_3H. [b] Run in Sutherland reactor.

The third-order reaction path has also been shown to be operative for the air oxidation of Fe(II) in aqueous sulfate and perchlorate medium[7] and of Pu(III) in sulfate solutions.[8] As suggested for the Fe(II) oxidation,[7] this order implies that the rate-determining step is the addition of O_2 to 2Cu(I).

$$O_2 + 2LiCuCl_2 \xrightarrow{\text{slow}} LiCl_2CuOOCuCl_2Li \qquad (2)$$

$$I + 2HOAc \xrightarrow{\text{fast}} 2LiOAc + 2CuCl_2 + H_2O_2 \qquad (3)$$

$$H_2O_2 + 2LiCuCl_2 + 2HOAc \xrightarrow{\text{fast}} 2LiOAc + 2CuCl_2 + 2H_2O \qquad (4)$$

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Metal Complexes of N,N,N′,N′-Tetramethylmalonamide

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Recent studies[2–5] of amides as ligands have involved various substituted monoamides which function as monodentate ligands. A search of the literature

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failed to reveal any comprehensive study of the donor characteristics of diamides. A number of studies have mentioned copper and nickel compounds of biuret and the use of malonamide in the "biuret reaction."[6–8] We have undertaken an investigation of the donor properties of N,N,N′,N′-tetramethylmalonamide (TMM). This diamide would be expected to be bidentate, forming six-membered chelate rings with metal ions. In this article we describe the preparation and characterization of nine metal perchlorate complexes of N,N,N′,N′-tetramethylmalonamide.

Experimental Section

Preparation of Compounds.—The N,N,N′,N′-tetramethylmalonamide was prepared in this laboratory by a method described by Lawson and Croom.[9] Diethylmalonate (1 mole), dimethylamine (5 moles), and a few drops of reagent hydrochloric acid (38%) were placed in a 1-l. autoclave and maintained at 150° for 8 hr. The amide was obtained by distillation at reduced pressure; bp 132° (2.5 mm), $n^{21}\text{D}$ 1.4903.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.15; H, 8.92; N, 17.71. Found: C, 52.96; H, 8.71; N, 17.79.

All of the metallic complexes of TMM except the chromium compound were prepared by nearly the same procedure. The hydrated metal perchlorate was treated at room temperature with an 80–100% excess of 2,2-dimethoxypropane[10] for a period of 2 hr. The resulting solution was then treated with a 3-fold mole ratio of the amide. The cobalt(II), nickel(II), lead(II), and copper(II) compounds precipitated immediately. These compounds were collected by filtration and then recrystallized by dissolving in ethanol and reprecipitating the complex by the dropwise addition of diethyl ether. The cadmium and manganese(II) compounds separated as oils upon the addition of the amide to the metal salt solution. Solidification of the oils was affected by repeatedly washing and stirring the oil with diethyl ether. The cadmium compound was recrystallized from ethanol. The manganese(II) compound decomposed upon attempted recrystallization.

The **iron(III)** and **zinc** compounds were prepared directly in ethanol from the hydrated perchlorate salts. To 0.005 mole of the hydrated metal perchlorate salt in 20 ml of absolute ethanol was added 0.015 mole of TMM. The iron(III) complex crystallized immediately. The solid zinc complex was obtained by adding an excess of diethyl ether. Both compounds were recrystallized from ethanol. The chromium(III) complex was prepared by the method described by Madan and Denk.[2]

The compounds were analyzed for C, H, and N by Weiler and Strauss Microanalytical Laboratory, Oxford, England, or by Galbraith Laboratories, Inc., Knoxville, Tenn. Metal analyses were done in this laboratory using EDTA titrations.[11] The melting points were obtained in open capillaries and are uncorrected.

Tris(N,N,N′,N′-tetramethylmalonamide)chromium(III) perchlorate is a dark green, slightly hygroscopic crystalline material; mp 252–253°.

Anal. Calcd for $[(Cr(C_7H_{14}N_2O_2)_3](ClO_4)_3$: C, 30.57; H, 5.13; N, 10.19; Cr, 6.30. Found: C, 30.42; H, 5.20; N, 10.27; Cr, 6.23.

Tris(N,N,N′,N′-tetramethylmalonamide)manganese(II) perchlorate is a white crystalline solid melting at 204–207° with decomposition. This compound is hygroscopic and decomposes in the presence of moisture and air.

Anal. Calcd for $[Mn(C_7H_{14}N_2O_2)_3](ClO_4)_2$: C, 34.62; H, 5.81, N, 11.54; Mn, 7.54. Found: C, 34.53; H, 5.93; N, 11.30; Mn, 7.47.

Tris(N,N,N′,N′-tetramethylmalonamide)iron(III) perchlorate is a yellow crystalline material melting at 183–185° with decomposition.

Anal. Calcd for $[Fe(C_7H_{14}N_2O_2)_3](ClO_4)_3$: C, 30.43; H, 5.11; N, 10.14; Fe, 6.74. Found: C, 30.17; H, 5.30; N, 9.82; Fe, 6.67.

Tris(N,N,N′,N′-tetramethylmalonamide)cobalt(II) perchlorate is a rose-pink, slightly hygroscopic crystalline material, melting at 217–219°.

Anal. Calcd for $[(Co(C_7H_{14}N_2O_2)_3](ClO_4)_2$: C, 34.43; H, 5.78; N, 11.48; Co, 8.05. Found: C, 34.09; H, 5.47; N, 11.58; Co, 8.16.

Tris(N,N,N′,N′-tetramethylmalonamide)nickel(II) perchlorate is a slightly hygroscopic, light green crystalline material melting at 250–251° with decomposition.

Anal. Calcd for $[Ni(C_7H_{14}N_2O_2)_3](ClO_4)_2$: C, 34.44; H, 5.78; N, 11.48; Ni, 8.02. Found: C, 34.16; H, 5.73; N, 11.29; Ni, 8.00.

Bis(N,N,N′,N′-tetramethylmalonamide)copper(II) perchlorate is a slightly hygroscopic, blue crystalline material melting at 218–221° with decomposition.

Anal. Calcd for $[Cu(C_7H_{14}N_2O_2)_2](ClO_4)_2$: C, 29.04; H, 4.88; N, 9.68; Cu, 10.98. Found: C, 29.45; H, 4.87; N, 10.15; Cu, 10.92.

Tris(N,N,N′ N′-tetramethylmalonamide)zinc(II) perchlorate is a white, slightly hygroscopic crystalline material melting at 205–207°.

Anal. Calcd for $[Zn(C_7H_{14}N_2O_2)_3](ClO_4)_2$: C, 34.13; H, 5.73; N, 11.38; Zn, 8.85. Found: C, 34.34; H, 5.64; N, 11.37; Zn, 8.84.

Tris(N,N,N′,N′-tetramethylmalonamide)cadmium(II) perchlorate is a light yellow, slightly hygroscopic crystalline material melting at 154–156°.

Anal. Calcd for $[Cd(C_7H_{14}N_2O_2)_3](ClO_4)_2$: C, 32.09; H, 5.39; N, 10.70; Cd, 14.32. Found: C, 32.02; H, 5.44; N, 10.45; Cd, 14.54.

Bis(N,N,N′,N′-tetramethylmalonamide)lead(II) perchlorate is a white crystalline solid melting at 219–221° with decomposition.

Anal. Calcd for $[Pb(C_7H_{14}N_2O_2)_2](ClO_4)_2$: C, 23.27; H, 3.91; N, 7.76; Pb, 28.68. Found: C, 23.36; H, 3.89; N, 7.60; Pb, 28.70.

Physical Measurements.—Infrared spectra were obtained as Nujol mulls in the 2–15 μ region using a Beckman Model IR-5A spectrophotometer. Electronic spectra in the visible and near-infrared regions of nitromethane solutions and Nujol mulls were obtained using a Cary Model 14 recording spectrophotometer.

Conductance measurements of nitromethane solutions were made using an Industrial Instruments Model RC-1 conductivity bridge and a conventional cell calibrated with 0.1 *M* KCl.

Magnetic susceptibilities were obtained on a Gouy balance at three field strengths on solid samples in Pyrex tubes which had been calibrated with mercury(II) tetrathiocyanatocobaltate(II).[12] Molar susceptibilities were corrected using tabulated diamagnetic corrections.[13] Magnetic moments were calculated using the Curie–Weiss law assuming a Curie temperature of 0°.

Results and Discussion

Conductance Measurements.—The conductances of solutions of these complexes in nitromethane are summarized in Table I. As might be expected for measurements in a solvent with a low dielectric constant, the molar conductance increases upon diluting the solution. The values given for the more dilute solu-

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TABLE I

INFRARED CARBONYL STRETCHING FREQUENCIES,[a] MAGNETIC MOMENTS, AND MOLAR CONDUCTIVITIES IN NITROMETHANE FOR COMPLEXES OF N,N,N′,N′-TETRAMETHYLMALONAMIDE

Compound	Carbonyl stretching[b] frequency, cm^{-1}	μ_{eff}, BM[c]	λ,[c] $cm^2\ ohm^{-1}\ mole^{-1}$
TMM	1645		
$[Cr(TMM)_3](ClO_4)_3$	1613	4.01	293 (0.236)[d]
			223 (1.18)
$[Mn(TMM)_3](ClO_4)_2$	1616	6.03	159 (2.74)
$[Fe(TMM)_3](ClO_4)_3$	1600	6.05	260 (0.258)
			191 (1.61)
$[Co(TMM)_3](ClO_4)_2$	1631	5.03	165 (3.00)
			117 (25.3)
$[Ni(TMM)_3](ClO_4)_2$	1621	3.31	170 (2.73)
			119 (25.6)
$[Cu(TMM)_2](ClO_4)_2$	1603	1.96	159 (1.75)
			134 (4.38)
$[Zn(TMM)_3](ClO_4)_2$	1621		170 (2.78)
$[Cd(TMM)_3](ClO_4)_2$	1610		169 (2.54)
$[Pb(TMM)_2](ClO_4)_2$	1645		168 (2.78)
	1610		
	1582		

[a] The assignment of this frequency to the carbonyl group is not intended to imply that absorption is due only to the C=O bond. Undoubtedly there are significant contributions from the C—N bond. [b] Reported values are believed to be correct to within ±3 cm^{-1}. [c] Values reported are for a temperature of 23°. [d] Numbers in parantheses are millimolar concentrations.

tions agree with reference values of 177 for a 2:1 complex and 262 for a 3:1 complex given by Gill and Nyholm.[14]

Infrared Spectra.—Table I gives a summary of the changes in the carbonyl stretching frequency upon coordination of the N,N,N′,N′-tetramethylmalonamide with the metal perchlorate. In every case this band is shifted to lower frequency indicating that the amide is coordinating through the oxygen of the carbonyl group.

TABLE II

NEAR-INFRARED AND VISIBLE SPECTRA OF SOME N,N,N′,N′-TETRAMETHYLMALONAMIDE COMPLEXES

Compound	Assignment	Nujol mull, max, cm^{-1}	Nitromethane solution, max, cm^{-1}	ϵ_{max}, l. $mole^{-1}\ cm^{-1}$
$[Cr(TMM)_3](ClO_4)_3$	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$	17,100	16,900	130
	$\rightarrow {}^4T_{1g}(F)$	23,500	23,100	103
	$\rightarrow {}^4T_{1g}(P)$	41,900	...	...
$[Co(TMM)_3](ClO_4)_2$	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	8,330	7,860	8.7
	$\rightarrow {}^4A_{2g}(F)$	(16,900)[a]	(17,000–16,000)	(3.0)
	$\rightarrow {}^4T_{1g}(P)$	18,900	18,600	29.1
		20,400[b]	20,140[b]	...
		21,400[b]		
$[Ni(TMM)_3](ClO_4)_2$	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	8,850	8,600	12.1
		13,700[b]	13,600[b]	7.4
	$\rightarrow {}^3T_{1g}(F)$	15,100	14,800	8.6
	$\rightarrow {}^3T_{1g}(P)$	26,600	25,200	22.3
$[Cu(TMM)_2](ClO_4)_2$	...	15,100[c]	14,300	26.6

[a] Very broad shoulder; value given is an estimate. [b] Shoulder. [c] Broad unsymmetrical absorption.

A triplet was observed for the carbonyl stretching vibration in the spectrum of the lead compound. The observation of a doublet upon coordination of structurally similar ligands has been discussed by Cotton.[15]

Magnetic Properties.—Table I also gives a summary of the magnetic properties of the N,N,N′,N′-tetramethylmalonamide complexes. The magnetic moments of the manganese, iron, and cobalt complexes are within the range expected for spin-free, weak-field octahedral complexes. The value of 3.31 BM for the nickel complex indicates an octahedral environment. A value 1.96 BM was obtained for the bis(N,N,N′,N′-tetramethylmalonamide)copper(II) perchlorate. The predicted moments for tetragonal and tetrahedral copper(II) complexes are very close together (1.91 BM for octahedral *vs.* 2.2 BM for tetrahedral).[16] Even though the measured magnetic moment agrees very well for the predicted value for copper(II) in a tetragonal field, an assignment of the structure of the compound on this basis would not be justified.

Visible and Near-Infrared Spectra.—The spectra obtained using nitromethane solutions and Nujol mulls of the complexes are given in Table II.

For these compounds a comparison of the spectra in the nitromethane and as Nujol mulls indicates that the primary absorbing species in solution is the same as in the solid. The spectrum of the copper complex in nitromethane differs slightly from its spectrum as a Nujol mull. It seems reasonable that the solid copper complex is square-planar, while in solution the copper-containing species could be six-coordinate involving two nitromethane molecules per copper. The spectra of the chromium, cobalt, and nickel compounds were typical of octahedral complexes in each case. Assignments of the electron transitions for the observed absorption bands were made on the basis of octahedral symmetry. Using the secular equations of Orgel[17] and the energy of the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition, a value of 14,260 cm^{-1} was calculated for the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition of tris(N,N,N′,N′-tetramethylmalonamide)nickel(II) perchlorate. This compares favorably with the experimental value of 14,800 cm^{-1}. Using this calculation the $E(P) - E(F)$ term lowering of tris(N,N,N′,N′-tetramethylmalonamide)chromium(III) perchlorate was calculated, but a check of the fit

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of the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ could not be made since nitromethane absorbs in the region of the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition. Although this transition could be observed in the spectrum obtained in the Nujol mull, it has been demonstrated by Schaffer[18] that this band deviates from the predicted position, possibly due to charge-transfer interactions, and therefore no calculation was made.

TABLE III

LIGAND FIELD PARAMETERS OF THE N,N,N′,N′-TETRAMETHYLMALONAMIDE COMPLEXES

Compound	Dq, cm^{-1}	$E(P) - E(F)$, cm^{-1}	β,[a] %
$[Cr(C_7H_{14}N_2O_2)_3](ClO_4)_3$	1690	9,020	34.3
$[Co(C_7H_{14}N_2O_2)_3](ClO_4)_2$	890	12,300	15.5
$[Ni(C_7H_{14}N_2O_2)_3](ClO_4)_2$	860	13,600	13.6

[a] The per cent lowering of the $E(P) - E(F)$ from that of the free-ion value.

For cobalt the values of the Dq and β were calculated on the basis of O_h symmetry. The ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition could not be resolved but showed up as a broad shoulder on the 18,600 cm^{-1} peak. This transition, which involves two electrons, would be expected to be of very weak intensity.[19]

For nickel(II) the Dq value of 860 cm^{-1} would place N,N,N′,N′-tetramethylmalonamide in the spectrochemical series near water (860 cm^{-1}). For chromium, N,N,N′,N′-tetramethylmalonamide has a Dq value (1690 cm^{-1}) less than that of water (1740 cm^{-1}).

The fact that N,N,N′,N′-tetramethylmalonamide gives larger Dq values than other amides is probably due to a chelate effect as it is a bidentate ligand. The chelate effect is illustrated by comparing the Dq values for nickel(II) of various monodentate ligands and similar bidentate ligands: pyridine (1010 cm^{-1})[20] *vs.* bipyridyl (1150 cm^{-1}),[21] pyridine N-oxide (840 cm^{-1})[22] *vs.* 2,2′-bipyridine-1,1′-dioxide (857 cm^{-1}),[23] methylamine (993 cm^{-1})[24] *vs.* ethylenediamine (1150 cm^{-1}).[25] N,N,N′,N′-Tetramethylmalonamide (860 cm^{-1}) may thus be compared with N,N-dimethylacetamide (769 cm^{-1}).[5] On this basis it is seen that there is a chelate effect. For chromium we also see a pronounced chelate effect when N,N,N′,N′-tetramethylmalonamide (1690 cm^{-1}) is compared with N,N-dimethylacetamide (1517 cm^{-1}).[5]

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The Preparation of Pentafluorosulfanylamine, SF_5NH_2

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Although several α-fluoro secondary amines R_fNHR_f' have been prepared, where R_f and R_f' have been either perfluoroalkyl[1-3] or pentafluorosulfanyl groupings, no α-fluoro primary amines have been reported to date. These secondary amines have generally been prepared by the addition of HF across the carbon–nitrogen bond of a perfluoroimino precursor, *e.g.*, $SF_5N{=}CF_2 + HF \rightarrow SF_5NHCF_3$. We have found that the primary amine SF_5NH_2 can be prepared by the addition of two molecules of HF across the sulfur–nitrogen triple bond[4] in thiazyl trifluoride,[5] NSF_3.

$$NSF_3 + 2HF \longrightarrow SF_5NH_2$$

Pentafluorosulfanylamine is a volatile white solid ($P_{0°} = 29$ mm). It dissociates to NSF_3 and HF slowly at room temperature and rapidly around 45° in the presence of small amounts of moisture. The amine can, however, be handled in a dry glass vacuum system if transfers are made rapidly, and it is stable when stored at −78°. It was found to be soluble in dry diethyl ether even at −78°.

Experimental Section

Reagents.—Thiazyl trifluoride, NSF_3, was obtained[6] as a product of the reaction of N-fluoroformyliminosulfur difluoride,[7] $F_2S{=}NCOF$, with silver difluoride (Harshaw Chemical Co.) and was purified by fractional condensation. The purity of the NSF_3 was confirmed by comparing its infrared spectrum with the published spectrum[5] and by vapor density molecular weight determination. Ultrapure hydrogen fluoride (furnished by the Blockson Chemical Division of Olin Mathieson Corp.) was used directly from the cylinder.

Reaction.—In a typical reaction 9.7 mmoles of NSF_3 and excess HF (143 mmoles) were held in a Kel-F tube reactor (2-cm diameter) for 18 hr at room temperature. (This length of time was arbitrary. Later experiments have indicated that the time required for the reaction to reach completion may actually be very much less.) The contents of this vessel were then distilled under vacuum to another Kel-F vessel packed with 25 g of NaF pellets and were allowed to sit over this NaF at room temperature for several hours to remove the unreacted HF from the sample. The volatiles after this treatment, 3.1 mmoles of SF_5NH_2 and 6.1 mmoles of NSF_3, were separated by passing the gases through two traps cooled to −63 and −196°, respectively. This represents a 34% yield of the amine.

General Methods.—Infrared spectra were studied using a Perkin-Elmer Model 137 Infracord spectrometer. The gaseous

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