Inorganica Chimica Acta, 31 (1978) 125–133
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Silver(I), Copper(I), Mercury(II) and Nickel(II) Halide and Perchlorate Complexes with N-Methylthiopyrrolidinone(2)

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Received March 16, 1978

The synthesis, electronic absorption spectra, magnetic susceptibilities as solids and in solution, infrared spectra and conductance measurements of the following complexes with N-methylthiopyrrolidinone(2) (NMTP) are described: $Ag(NMTP)_2Cl$, $Ag(NMTP)_2Br$, $Ag(NMTP)I$, $Ag(NMTP)_4ClO_4$, $Ag(NMTP)_4NO_3$, $Cu(NMTP)_2Cl$, $Cu(NMTP)_2Br$, $Cu(NMTP)_2I$, $Cu(NMTP)_4ClO_4$, $Hg(NMTP)_2Cl_2$, $Hg(NMTP)_2Br_2$, $Hg(NMTP)_2I_2$, $Hg(NMTP)_5(ClO_4)_2$, $Ni(NMTP)_2Cl_2$, $Ni(NMTP)_2Br_2$, $Ni(NMTP)_2I_2$ *and* $Ni(NMTP)_4(ClO_4)_2$. *The nature of interaction, the coordination in the crystalline state and in solution and the dissociation of the complexes in NMTP are discussed.*

Introduction

Studies on the redox behaviour of cations in N-methylthiopyrrolidinone(2) [NMTP] have shown that a strong interaction between Ag^+ as well as Cu^+ and NMTP exists [1]. Thus silver halides are quite soluble in NMTP. Since complexes of Ag^+ with another sulfur containing solvent, namely N,N-dimethylthioformamide have been prepared recently [2], it was of interest to prepare and study complexes of silver salts with NMTP. These studies were expanded to investigate the possibility of copper and mercury complexes with this ligand. It was of particular interest whether complexes of both Cu^{2+} and Cu^+ as well as Hg_2^{2+} and Hg^{2+} were obtainable. Finally studies on complexes with nickel halides and perchlorate were included in this paper.

Experimental

N-methylthiopyrrolidinone(2) [NMTP] was prepared by reacting commercially available N-methylpyrrolidinone(2) with P_2S_2 in a procedure described previously [1].

$Ag(NMTP)_2Cl$, $Ag(NMTP)_2Br$, $Ag(NMTP)I$, $Ag(NMTP)_4ClO_4$, $Ag(NMTP)_4NO_3$, $Cu(NMTP)_2Cl$, $Cu(NMTP)_2Br$, $Cu(NMTP)_2I$, $Hg(NMTP)_2Cl_2$, $Hg(NMTP)_2Br_2$, were obtained by dissolving the anhydrous metal halides, nitrates and perchlorate respectively in NMTP at 100 °C under nitrogen. Upon cooling to room temperature the white crystals were filtered and washed with diethylether under a nitrogen atmosphere. The compounds were dried at room temperature and 0.1 Pa.

$Cu(NMTP)_4ClO_4$ was prepared by dissolving $Cu(ClO_4)_2 \cdot 2H_2O$ in NMTP as described above. The solution turned yellow, cooling to room temperature yielded upon washing with diethylether white crystals. The compound was diamagnetic proving that a reduction of Cu^{2+} during this procedure had occurred.

Since direct reaction of $Hg(ClO_4)_2 \cdot 3H_2O$ with NMTP led to black unidentified products, $Hg(NMTP)_5(ClO_4)_2$ was obtained by reaction bistriphenylphosphinemercury(II) perchlorate [3] with an excess of NMTP. White crystals were obtained.

$Hg(NMTP)_2I_2$ was prepared by a method similar to that used for $Hg(NMTP)_2Cl_2$ and $Hg(NMTP)_2Br_2$. The crystals however could not be washed with diethylether since $Hg(NMTP)_2I_2$ is quite soluble in diethylether. Recrystallisation from nitromethane was employed as the final purification step.

Efforts to prepare complexes with Hg_2^{2+} and NMTP failed, since Hg_2^{2+} disproportionates in NMTP yielding mercury and the NMTP complex with Hg^{2+}.

The melting points, the ranges of thermal decomposition and the analysis of these compounds are given in Table I.

$Ni(NMTP)_2Cl_2$ as made by reacting anhydrous $NiCl_2$ and NMTP at 100 °C under dry nitrogen. Blue-green crystals were obtained at room temperature. This compound was found to be hygroscopic. Attempts to recrystallize this compound from dichloromethane, nitromethane and trichloromethane led to the decomposition of this complex. Solvents such as aceton, acetonitrile, butanol and water replaced NMTP as ligand.

$Ni(NMTP)_2Br_2$ obtained as described for the silver complexes could be recrystallized either from acetonitrile or acetone yielding green crystals.

$Ni(NMTP)_2I_2$ made from NiI_2 and NMTP yielded a brown oily product when crystallized from NMTP. Recrystallization from acetonitrile gave dark brown

TABLE I. Molecular Weights, Melting Points and Decomposition Ranges respectively, as well as the Analysis of Silver, Copper and Mercury Complexes with N-methylthiopyrrolidinone(2).

Compound	°C	Molecular Weight		C	H	N	S	Halides	Hg
$Ag(NMTP)_2Cl$	70–71	373.72	calc.	32.13	4.85	7.50	17.16	9.49	
			found	32.29	4.81	7.49	17.77	9.84	
$Ag(NMTP)_2Br$	60–130[a]	418.18	calc.	28.72	4.33	6.70	15.34	19.10	
			found	28.30	4.26	6.58	15.49	19.32	
$Ag(NMTP)I$	154–155	349.97	calc.	17.15	2.59	4.00	9.16	36.26	
			found	17.25	2.50	3.97	9.74	36.14	
$Ag(NMTP)_4ClO_4$	49–51	668.11	calc.	35.95	5.43	8.39	19.20	5.31	
			found	36.08	5.50	8.44	19.44	5.57	
$Ag(NMTP)_4NO_3$	59–60	630.67	calc.	38.09	5.75	11.10	20.34	–	
			found	37.90	5.88	11.00	20.25	–	
$Cu(NMTP)_2Cl$	115	329.39	calc.	36.43	5.46	8.50	19.47	10.77	
			found	36.79	5.48	8.55	19.44	11.17	
$Cu(NMTP)_2Br$	114–116	373.85	calc.	32.10	4.81	7.49	17.15	21.37	
			found	32.37	4.73	7.48	17.60	21.91	
$Cu(NMTP)_2I$	99	420.84	calc.	28.51	4.28	6.65	15.24	30.16	
			found	28.66	4.28	6.69	15.85	30.05	
$Cu(NMTP)_4ClO_4$	79	623.78	calc.	38.51	5.82	8.98	20.56	5.68	
			found	38.50	5.77	8.94	20.63	5.84	
$Hg(NMTP)_5(ClO_4)_2$	90–150[a]	975.48	calc.	30.78	4.65	7.18	16.44	–	20.57
			found	30.86	4.59	7.37	17.12	–	20.77
$Hg(NMTP)_2Cl_2$	125–126	501.89	calc.	23.93	3.62	5.58	12.78		
			found	24.16	3.47	5.96	13.20		
$Hg(NMTP)_2Br_2$	114–115	590.80	calc.	20.33	3.07	4.74	10.85		
			found	20.64	3.04	4.87	11.41		
$Hg(NMTP)_2J_2$	114–116	684.80	calc.	17.54	2.65	4.09	9.37		
			found	17.58	2.54	4.42	9.70		

[a] Decomposition.

TABLE II. Molecular Weights and Analysis of Nickel Complexes with N-methylthiopyrrolidinone(2).

Compound	Molecular Weight		C	H	N	S	Halide	Ni
$Ni(NMTP)_2Cl_2$	360.01	calc.	33.36	5.04	7.78	17.81	19.70	16.3
		found	32.81	5.90	7.39	18.30	19.19	14.9
$Ni(NMTP)_2Br_2$	448.92	calc.	26.75	4.04	6.24	14.29	35.60	13.07
		found	26.82	4.02	6.24	14.15	35.74	12.80
$Ni(NMTP)_2I_2$	542.90	calc.	22.12	3.34	5.16	11.81	46.75	10.81
		found	22.21	3.31	5.09	11.94	46.10	10.73
$Ni(NMTP)_4(ClO_4)_2$	718.40	calc.	33.44	5.05	7.80	17.85	9.87	8.17
		found	33.09	5.02	7.67	17.81	9.97	7.84

crystals. $Ni(NMTP)_2I_2$ could also be prepared by reacting NiI_2 and NMTP in stoichiometric amounts in acetonitrile.

$Ni(NMTP)_4(ClO_4)_2$: Two procedures were developed to prepare the compound. The first one consisted of dissolving the $Ni(ClO_4)_2 \cdot 2H_2O$ in hot NMTP. Dark green crystals were obtained from a yellow brown solution. The crystals were filtered, washed with diethylether and recrystallized from nitromethane. The alternative route consisted in stirring a $Ni(ClO_4)_2 \cdot 6H_2O$ solution in dimethoxypropane (100% excess) at room temperature for two hours before adding the stoichiometric amount of NMTP. The $Ni(NMTP)_4(ClO_4)_2$ precipitate was washed with diethylether and dried at room temperature and 0.1 Pa. $Ni(NMTP)^4(ClO_4)_2$ decomposed in dichloromethane. In chloroform, acetone, acetonitrile and water the solvent molecules replaced NMTP as a ligand.

All nickel complexes decomposed at temperatures above 140 °C. The nickel content was analyzed by a complexometric titration [4]. The analysis of these compounds is given in Table II.

TABLE III. Equivalent Conductivities λ_c [Ω^{-1} cm^2 eq^{-1}] and Concentrations c [mol dm^{-3}] of Silver, Copper, Mercury and Nickel Complexes with N-methylthiopyrrolidinone(2) [NMTP] in NMTP as a Solvent.

$c \times 10^4$	λ_c	$c \times 10^4$	λ_c	$c \times 10^4$	λ_c	$c \times 10^4$	λ_c
$Ag(NMTP)_2Cl$		$Ag(NMTP)I$		$Ag(NMTP)_4NO_3$		$Cu(NMTP)_2Br$	
0.643	15.34	1.003	14.30	1.240	16.727	1.433	14.997
1.680	14.95	1.702	13.79	2.784	16.707	2.187	14.870
2.848	14.39	2.457	13.29	4.074	16.661	2.974	14.754
3.872	13.79	3.189	12.86	5.301	16.588	4.068	14.459
4.797	13.59	3.602	12.64	6.708	16.527	5.101	14.430
6.050	13.14	4.239	12.34	8.870	16.425	5.639	14.359
7.053	12.82	4.839	12.06	10.318	16.377	6.332	14.269
8.436	12.41	5.586	11.78	12.290	16.303	7.206	14.150
10.440	11.95	6.214	11.53			7.971	14.045
12.504	11.50	6.837	11.31			8.855	13.942
14.196	11.18	7.656	10.97			9.904	13.822
		8.445	10.69				
$Ag(NMTP)_2Br$		$Ag(NMTP)_4ClO_4$		$Cu(NMTP)_2Cl$		$Cu(NMTP)_2I$	
1.876	14.75	1.562	15.51	0.632	14.217	1.206	14.960
3.234	14.15	2.356	15.44	1.616	13.546	1.565	14.938
4.891	13.53	3.336	15.37	2.181	13.130	2.281	14.878
6.430	13.03	4.651	15.28	2.650	12.813	2.646	14.834
7.774	12.65	5.686	15.23	3.073	12.551	2.855	14.815
8.900	12.36	6.811	15.16	3.483	12.308	3.430	14.786
10.425	12.01	7.431	15.13	3.976	12.044	3.852	14.720
11.315	11.82	8.261	15.09	4.485	11.779		
12.410	11.60	9.425	15.04	4.922	11.585		
14.200	11.28	10.347	14.99	5.495	11.355		

$c \times 10^4$	λ_c	$c \times 10^4$	λ_c	$c \times 10^4$	λ_c
$Cu(NMTP)_4ClO_4$		$Ni(NMTP)_2Cl_2$		$Ni(NMTP)_2I_2$	
1.725	15.754	0.726	0.630	1.770	8.020
2.193	15.735	1.412	0.588	2.638	7.567
2.905	15.690	2.660	0.560	3.740	7.216
3.594	15.643	2.960	0.558	4.684	6.993
4.257	15.597	3.376	0.551	5.405	6.840
4.683	15.555	3.723	0.563	6.050	6.740
5.403	15.525	4.136	0.559	6.826	6.620
5.881	15.506	4.490	0.556	7.460	6.530
6.725	15.467	4.810	0.554	8.250	6.426
7.300	15.417			8.888	6.354
				9.706	6.265
$Hg(NMTP)_5(ClO_4)_2$		$Ni(NMTP)_2Br_2$		$Ni(NMTP)_4(ClO_4)_2$	
0.475	18.154	1.458	3.330	0.633	17.81
0.664	18.112	1.900	3.040	0.929	17.71
0.912	18.020	2.524	2.741	1.331	17.58
1.193	17.935	3.135	2.513	1.724	17.46
1.452	17.850	3.679	2.411	2.050	17.35
1.774	17.740	4.193	2.291	2.400	17.23
2.147	17.610	4.697	2.189	2.645	17.15
2.421	17.536	5.388	2.072	2.996	17.07
2.702	17.449	5.802	2.012	3.308	16.99
2.863	17.406	6.230	1.955	3.526	16.94
3.046	17.357	6.700	1.899	3.783	16.87
				4.023	16.82

(continued overleaf)

TABLE III. *(continued)*

$c \times 10^4$	λ_c	$c \times 10^4$	λ_c	$c \times 10^4$	λ_c
$Hg(NMTP)_2Cl_2$		$Hg(NMTP)_2Br_2$		$Hg(NMTP)_2I_2$	
1.507	2.002	1.346	2.395	0.956	1.901
2.713	1.638	1.776	2.143	1.592	1.547
4.205	1.392	2.518	1.853	2.260	1.339
5.370	1.269	3.264	1.662	2.767	1.232
6.456	1.182	3.814	1.556	3.384	1.134
7.338	1.126	4.495	1.451	3.378	1.061
8.158	1.082	5.160	1.368	4.651	0.995
8.960	1.046	5.752	1.305	5.280	0.946
		6.216	1.263	5.800	0.912
		6.782	1.218		
		7.365	1.177		

TABLE IV. Dissociation Constants and λ_0 Values of Silver and Copper Complexes in N-methylthiopyrrolidinone(2) Employing Crystallographic Radii and the Bjerrum Constant (Dielectric Constant: 47.5).

Compound	Bjerrum Constant 590 pm		Crystallographic Radii		
	λ_0 $[\Omega^{-1}\ cm^2\ eq^{-1}]$	K_{diss}	r [pm]	λ_0 $[\Omega^{-1}\ cm^2\ eq^{-1}]$	K_{diss}
$Ag(NMTP)_2Cl$	16.12	2.53×10^{-3}	307	16.12	2.51×10^{-3}
$Ag(NMTP)_2Br$	16.22	2.56×10^{-3}	322	16.22	2.54×10^{-3}
$Ag(NMTP)I$	15.57	1.43×10^{-3}	346	15.57	1.42×10^{-3}
$Cu(NMTP)_2Cl$	15.19	1.36×10^{-3}	277	15.19	1.35×10^{-3}
$Cu(NMTP)_2Br$	15.51	1.37×10^{-2}	292	15.51	1.36×10^{-2}
$Ag(NMTP)_4ClO_4$	15.86				
$Ag(NMTP)_4NO_3$	17.18				
$Cu(NMTP)_2I$	15.28				
$Cu(NMTP)_4ClO_4$	16.13				

Apparatus

The UV–visible spectra were measured on a Cary 17 D spectrophotometer. Solution spectra were recorded in 1 mm and 10 mm quartz cuvettes. Solid spectra were obtained from nujol mulls on filter paper according to a published method [5].

Magnetic moments of the solid nickel complexes were obtained on high precision Faraday balance SUS 10 (Anton Paar Company, Graz, Austria).

Measurements of the magnetic moments in solution were carried out on a Perkin Elmer R 12 A-NMR Spectrometer, the calculations of which were carried out according to a published method [6, 7].

Infrared spectra were recorded on a Perkin Elmer 180 IR-Spectrophotometer. KBr pellets were used for the range from 4 000 to 300 cm^{-1}, whereas Nujol mulls and polyethylene windows were used in the range from 525 to 32 cm^{-1}.

Conductivity measurements were made by means of a Wayne–Kerr autobalance universal bridge B 642. Polished platinum electrodes were used; the cell constant, calibrated in an aqueous KCl solution, was 0.3583 cm^{-1}. Solutions of the electrolyte were prepared in a glove box and added to a known volume of NMTP in the conductivity cell through a silicon septum by means of gas tight syringes (Hamilton). The added amount was measured by weighing the syringe before and after adding. All measurements were carried out at 25 + 0.02 °C under dry nitrogen.

Results

The concentrations (mol dm^{-1}) and equivalent conductivity values (λ_c) for the 1:1 and 1:2 electrolytes in NMTP are given in Table III. Based on these

TABLE V. Infrared Spectrum of N-methylthiopyrrolidinone(2) and Peak Position of Two IR Peaks that shift Significantly upon Coordination of the Complexes Studied.

Compound								
NMTP	2930 v.st, 2880 v.st, 1685 w, *1525 v.st,* 1465 st, 1450 st, 1420 m, 1395 m, 1315 v.st, 1250 m, 1220 m, *1123 st,* 1095, 1050 w, 1010 m, 950 m, 930 m, 850 m, 695 m, 602 st, 535 st v.st = very strong, st = strong, m = medium, w = weak							
$Ag(NMTP)_2Cl_2$	1120,	1539	$Cu(NMTP)_2Br$	1110,	1557	$Hg(NMTP)_5(ClO_4)_2$	[a]	
$Ag(NMTP)_2Br_2$	1119,	1555	$Cu(NMTP)_2I$	1110,	1557	$Ni(NMTP)_2Cl_2$	1117,	1570
$Ag(NMTP)I$	1121,	1555	$Cu(NMTP)_4ClO_4$	1115[b],	1545	$Ni(NMTP)_2Br_2$	1118,	1575
$Ag(NMTP)_4ClO_4$	[a]	1545	$Hg(NMTP)_2Cl_2$	1110,	1575	$Ni(NMTP)_2I_2$	1113,	1568
$Ag(NMTP)_4NO_3$	1117,	1555	$Hg(NMTP)_2Br_2$	1108,	1560	$Ni(NMTP)_4(ClO_4)_2$	[a]	1580
$Cu(NMTP)_2Cl$	1112,	1555	$Hg(NMTP)_2I_2$	1110,	1562			

[a] Masked by perchlorate. [b] Shoulder of ClO_4^- band.

data the dissociation constants of the 1:1 electrolytes have been calculated according to the procedure described by Fuoss and Krauss [8, 9]. Both the sum of the crystallographic radii and the Bjerrum radii have been used in these calculations and the results are given in Table IV. No difference in λ_o values using the crystallographic radii and the Bjerrum distance was found and only marginal variations in the dissociation constants occurred. Thus for the complexes studied the dissociation constants do not depend much on the distance chosen in this procedure. The dielectric constant of NMTP used was 47.5 and the viscosity 4.25 X 10^{-3} kg m^{-1} s^{-1} [1]. The specific conductivity of the solvent was 9.3 X 10^{-9} Ω^{-1} cm^{-1}. Ag $(NMTP)_4ClO_4$, $Ag(NMTP)_4NO_3$, $Cu(NMTP)_4ClO_4$ and $Cu(NMTP)_2I$, were strongly dissociated prohibiting a calculation of dissociation constants with the Fuoss–Krauss method. Since rigorous calculations of dissociation constants of 1:2 electrolytes based on conductivity measurements are not yet available, the conductivity data obtained for the mercury(II) and nickel(II) complexes could only be used as a qualitative measure of the dissociation of these complexes. A linear dependence of the equivalent conductivity (λ_c, Ω^{-1} cm^2 eq^{-1}) on the molar concentration (mol dm^{-3}) has been observed for both $Ni(NMTP)_4(ClO_4)_2$ and $Hg(NMTP)_5(ClO_4)_2$. The extrapolated λ_o values were 18.53 for $Ni(NMTP)_4(ClO_4)_2$ and 18.76 for $Hg(NMTP)_5(ClO_4)_2$. The slopes of the plots were in units mentioned above, –84.5 for $Ni(NMTP)_4(ClO_4)_2$ and –78.6 for the $Hg(NMTP)_5(ClO_4)_2$. Since λ_o values for single ions are not available in NMTP, Waldens rule was employed to get some information on λ_o values in NMTP from data in aqueous [10] and nonaqueous solutions [11]. A value of 10 was calculated for Ni^{2+} and 9 for ClO_4^- in NMTP. No reliable data were found for Hg^{2+} in any solvent, the λ_o values of Zn^{2+} and Cd^{2+} [10] in water have been used to get some idea on the λ_o value of Hg^{2+} in NMTP using Waldens rule. Such considerations lead to a value of 11 for Hg^{2+} in NMTP. Based on these data a λ_o value of 19 was calculated for $Ni(NMTP)_4(ClO_4)_2$ and of 20 for $Hg(NMTP)_5(ClO)_4$. Calculations of the Onsager slope based on the above mentioned λ_o values for the single ions gave –71.2 for $Ni(NMTP)_4(ClO_4)_2$ and –71.4 for $Hg(NMTP)_5(ClO_4)_2$. The agreement between calculated and experimental values is quite good considering the uncertainties in the λ_o values obtained via the Walden rule. This indicates that both $Ni(NMTP)_4(ClO_4)_2$ and $Hg(NMTP)_5(ClO_4)_2$ are strongly dissociated in NMTP. The halide complexes of both nickel and mercury with NMTP, as can be seen from the conductivity data in Table III, are only very weakly dissociated in NMTP.

The infrared spectrum of NMTP is given in Table V. Two bands were found to shift significantly upon complex formation and are listed in Table V. The far infrared spectra of all compounds studied are listed in Table VI.

The magnetic moments of the nickel complexes were measured as solids, in NMTP solutions containing 10 vol% benzene and in nitromethane containing 10 vol% dichloromethane. The data are listed in Table VII. No data for $Ni(NMTP)_2Cl_2$ in nitromethane could be obtained since this compound decomposes in this solvent. The diamagnetic molar susceptibility of NMTP was measured and found to be –76.09 X 10^{-6} [cm^3 mol^{-1}]. This value was used for all corrections.

UV–visible near IR spectra of the nickel complexes with NMTP were measured in NMTP nitromethane and as solids in nujol mulls. Peak positions and absorption coefficients are listed in Table VIII.

Discussion

NMTP as a donor molecule will interact with cations predominantly via the sulfur atom. Employ-

TABLE VI. Far Infrared Spectra of N-methylthiopyrrolidinone(2) [NMTP] and of Silver(I), Copper(I), Mercury(II) and Nickel(II) Complexes with NMTP[a].

Compound	ν [cm^{-1}]							
NMTP		501	382			274	226	
$Ag(NMTP)_2Cl$		497	386			297	250	163 (w) 132 (w)
$Ag(NMTP)_2Br$	510 (sh)	498	384			296	258	155
$Ag(NMTP)I$	516	497	386		307		240	142 (sh, w)
$Ag(NMTP)_4NO_3$	518	500	385			297	253	163 (w) 132 (w)
$Ag(NMTP)_4ClO_4$	515 (sh, w)	500	385			297	252	≈100 (br)
$Cu(NMTP)_2Cl$	515 (sh)	500	388	326 (w)	301 (w)		215	116 (w) 102 (w)
$Cu(NMTP)_2Br$		498	385	327	318		262	198, 181 (w), 151 (w) 120
$Cu(NMTP)_2I$	516	498	388	330 (sh)	320		254	170, 140, 118 (w)
$Cu(NMTP)_4ClO_4$		500	388		301		248	114, 95
$Hg(NMTP)_2Cl_2$		497	388		318	244	229 (br)	150 (w), 93 (br)
$Hg(NMTP)_2Br_2$		490	385		311		261, 167	147 (w, sh), 104
$Hg(NMTP)_2I_2$		500, 492	385		313		256	148 (br), 125
$Hg(NMTP)_5(ClO_4)_2$		505, 493	388		312	272	240 (sh)	147
$Ni(NMTP)_2Cl_2$	520 (sh)	496	388	345	310	282	201	122, 97
$Ni(NMTP)_2Br_2$		494	388	344			248, 211	90 (br)
$Ni(NMTP)_2I_2$		499 (sh) 491	388	346			259, 218	192, 140, 98
$Ni(NMTP)_4(ClO_4)_2$		493	385 (w)	362 (w)	324	270		196

[a] sh: shoulder, w: weak, br: broad.

TABLE VII. Magnetic Moments of Nickel Complexes with N-methylthiopyrrolidinone(2) as Solids and in Solution of Nitromethane with 10 vol% Dichloromethane and N-methylpyrrolidinone(2) with 10 vol% Benzene (magnetic moments in Bohr magneton).

Compound	Solids 293 °K	N-Methylpyrrolidinone(2) 308 °K	Nitromethane 308 °K
$Ni(NMTP)_2Cl_2$	3.32	3.27	Decomposition
$Ni(NMTP)_2Br_2$	3.44	3.31	3.59
$Ni(NMTP)_2I_2$	3.34	3.28	3.44
$Ni(NMTP)_4(ClO_4)_2$	3.37	3.41	3.49

ing Pearson's concept of hard and soft acids and bases (donor and acceptors) [12] as a classification scheme, NMTP will act as a soft donor. From the three classification schemes for cations, according to Schwarzenbach [13], Arhland, Chatt and Davies [14] and Pearson [12], Pearson's nomenclature will be used in this discussion. Interactions of NMTP with typically soft cations such as Ag^+, Cu^+ and Hg^{2+} should be strong. The excellent solubility of the silver salts including the silver halides is an excellent example of such soft–soft interactions. The complexes $Ag(NMTP)_2Cl$, $Ag(NMTP)_2Br$ and $Ag(NMTP)I$ are of similar composition as the silver halide complexes of N,N-dimethylthioformamide [DMTF], namely $Ag(DMTF)_2Cl$, $Ag(DMTF)_2Br$ and $Ag(DMTF)I$ [2].

Structural data derived from single crystal X-ray studies are available for DMTF complexes, showing tetrahedral coordination of the silver ion in all complexes [15]. One sulfur atom acts as a bridge in the silver chloride and the bromide complexes of DMTF. Similar structures have also been observed in the case of the thiourea complex $Ag(CH_4N_2S)_2Cl$ [16] and in the case of the N-methylthiourea $Ag(C_2H_6N_2S)_2Cl$ [17]. Thus a tetrahedral coordination by three sulfur and one halogen atom may be assumed for the complexes $Ag(NMTP)_2Cl$ and $Ag(NMTP)_2Br$. A tetrahedral coordination of three iodine atoms and one sulfur atom around the silver ion as observed in Ag(DMTF)I [15] is likely to occur also in the complex Ag(NMTP)I.

For both $Ag(NMTP)_4ClO_4$ and $Ag(NMTP)_4NO_3$ the coordination sites around the silver ion will be taken by sulfur atoms. Structural data are available for the complex of silver chloride with thioacetamide $Ag(C_2H_5NS)_4Cl$ [18]. The silver ion in this com-

TABLE VIII. UV–visible –near IR Spectra of Nickel Complexes with N-methylthiopyrrolidinone(2) in N-methylthiopyrrolidinone, in Nitromethane and as Nujol Mulls[a].

N-Methylthiopyrrolidinone(2)		Nitromethane		Nujol Mulls	
cm^{-1}	ϵ	cm^{-1}	ϵ	cm^{-1}	
		$Ni(NMTP)_4(ClO_4)_2$			
8330	23				
14490	368	14490	277	14490–15870	broad peak
15340	363	15270	283		
21410	4140	22000	3083	21910	
25970	7692	26320	5402		
		$Ni(NMTP)_2Cl_2$			
9090	48	decomposition			
10530 sh	25 sh				
14750 sh	152 sh				
15625	174			15380	
26080	1373				
		$Ni(NMTP)_2Br_2$			
8930	72	8930	61		
9740	58	9710	47		
10100	62	10050 sh	43 sh	13160–15150	broad peak
		13890 sh	206 sh		
15106	276	15000	225		
		25000 sh	2038 sh		
26110	3800	27780	4435		
		$Ni(NMTP)_2I_2$			
8770 sh	65 sh	8695	79		
10100	133	9370	111		
10420	131			12500–14300	broad peak
14880	416	13890	409		
21600	3490	20410	2700		
26000	5740	23750	3850		

[a] sh: shoulder.

pound is coordinated by four sulfur atoms. The infrared spectrum of $Ag(NMTP)_4ClO_4$ did not show any splitting of the ClO_4^- band at 1080 cm^{-1}. Since splitting of this band has been observed in case of coordination of the ClO_4^- ion [19], it can be concluded that the ClO_4^- does not coordinate to the silver ion.

The coordination via the sulfur atom is supported by a shift of the –C=S stretching frequency [20, 21] to lower frequencies (Table V). This indicates a weakening of the C=S bond due to coordination of the silver ion to the sulfur. Such a shift could be observed in all complexes but the perchlorates. In perchlorates the C=S stretching band is masked by the ClO_4^- band.

Conductivity measurements on the silver complexes show that in solution both $Ag(NMTP)_4ClO_4$ and $Ag(NMTP)_4NO_3$ are strongly dissociated, whereas the silver halide complexes are only weakly dissociated. This supports the concept that the halides are ligands not only in the crystals but also in solution. The dissociation constants decrease as observed on the DMTF complexes in the order $Ag(NMTP)_2Cl$, $Ag(NMTP)_2Br$ and $Ag(NMTP)I$. The corresponding NMTP complexes are less dissociated than the DMTF complexes [2].

The very rapid reduction of copper(II) perchlorate in NMTP is a good example of the much stronger interaction of a soft donor ligand with the soft acceptor Cu^+ than with the hard acceptor Cu^{2+}. An oxidation of the ligand is the most likely corresponding oxidation reaction, no efforts to elucidate the nature of the oxidation reaction were undertaken. Tetrahedral coordination of Cu^+ by four sulfur atoms has been observed in the thioacetamide complex $Cu(C_2H_5NS)_4Cl$ [18]. Similar coordination is likely in $Cu(NMTP)_4ClO_4$. Although no structural data of copper(I) halide complexes of the type CuL_2X are available at this time, it may be assumed that tetrahedral coordination will exist in these complexes similar to the silver chloride complex with N,N-dimethylthioformamide.

Copper(I) halides, poorly soluble in water, are very soluble in NMTP. Conductometric studies showed that both the iodide and the perchlorate are strongly dissociated in NMTP. The dissociation decreases in the order $Cu(NMTP)_2I$, $Cu(NMTP)_2Br$ and $Cu(NMTP)_2Cl$ contrary to the order of the dissociation of silver halides.

Efforts were made to prepare both complexes with Hg^{2+} and Hg_2^{2+} but only Hg^{2+} complexes with NMTP were obtained. This agrees with previous observations [22] that Hg^{2+} is a better acceptor for soft donor ligands than Hg_2^{2+}. Reaction with Hg_2Cl_2 led to a disproportionation reaction yielding metallic mercury and $Hg(NMTP)_2Cl_2$. Conductometric studies showed that only $Hg(NMTP)_5(ClO_4)_2$ is strongly dissociated in solution. In all other mercury complexes with NMTP the halide ions act predominantly as ligands. Based on the conductivity data given in Table III the degree of dissociation decreases in the order $Hg(NMTP)_2Cl_2$, $Hg(NMTP)_2Br_2$ and $Hg(NMTP)_2I_2$. Lack of both a suitable mathematical treatment of the dissociation of 1:2 electrolytes and experimental limiting equivalent conductivities of single ions in NMTP prevent calculations of dissociation constants. It is hoped that such calculations will become available in the future.

Both the copper and the mercury just as the silver and nickel complexes show a lowering of the C=S stretching frequency as compared to the pure NMTP, supporting the assumption of coordination of the metal ions to the sulfur (Table V). The band at 1530 cm^{-1} shows a shift to higher frequencies upon complex formation. This band has not been assigned unambiguously. A band at this position in N,N-dimethylthioformamide has been assigned to a C–N stretching frequency [23]. Such an assignment for the band at 1530 cm^{-1} in NMTP seems reasonable. A decrease in strength of the C=S bond should lead to an increase in strength of the C–N bond [24].

As observed with all other complexes studied, the perchlorate complex $Ni(NMTP)_2(ClO_4)_2$ was found to be strongly dissociated in NMTP. The halide complexes of nickel however contain the halides as ligands and are only weakly dissociated. The dissociation decreases in the order $Ni(NMTP)_2I_2$, $Ni(NMTP)_2Br_2$ and $Ni(NMTP)Cl_2$.

Since the nickel perchlorate complex with the oxygen analogous N-methylpyrrolidinone(2) (NMP), namely $Ni(NMP)_6(ClO_4)_2$ has octahedral coordination [25, 26] measurements of magnetic moments and electronic absorption spectra were made to obtain information on the type of coordination. Nickel halide complexes with N-methylpyrrolidinone(2) have only been mentioned in a patent [27]. A compound of the composition $Ni(NMP)_3Br_2$ is claimed as well as a nickel chloride complex with NMP of unknown composition. Octahedral, tetrahedral and square planar complexes are most often found for nickel compounds. Since truly square planar complexes of nickel are diamagnetic, the nickel compounds made in this study are either octahedral or tetrahedral. The magnetic moments although considerably higher than pure spin moments of 2.83 Bohr magneton are on the borderline of the values found for octahedral and tetrahedral coordination. The absorption peaks at 8000–9000 cm^{-1} and at about 15000 cm^{-1} agree well with the positions calculated for the $T_1(F) \rightarrow A_2$ and the $T_1(F) \rightarrow T_1(P)$ transitions required for tetrahedral coordination. The absorption coefficients of 150 to 400 observed for the peaks at about 15000 cm^{-1} are considerably higher than those usually observed for octahedral coordination and suggest tetral coordination. A comparison of the spectra in NMTP, nitromethane and in nujol mulls shows that the same species is present in all three environments.

Acknowledgements

Thanks are due to the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (Project 3004) for generous financial support. The authors are especially indebted to Dr. Rudolf Sobcak for his comments and his help during the measurements of the magnetic moments.

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