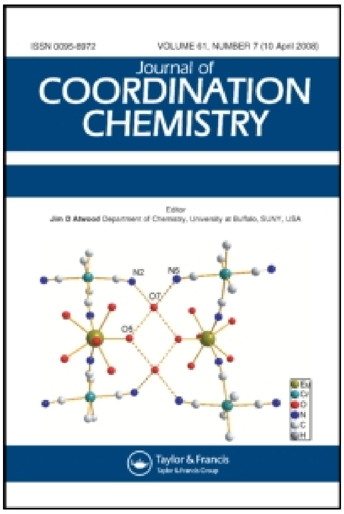

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METAL(II)-SOLVATES WITH N-ACETYLPYRROLIDINONE AS THE LIGAND: METAL-ION-INDUCED VIBRATIONAL DEGENERATION

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Seven new coordination compounds are reported with N-acetylpyrrolidinone (NAP) as the bidentate oxygen-donor ligand, viz. $[M(NAP)_3](SbCl_6)_2$ with M is Mg, Mn, Co, Ni, and Zn, and $[M(NAP)_3](InCl_4)_2$ with M is Co and Ni. The divalent metal ions are in a regular octahedral environment of six oxygen atoms. The amidic and the ketonic carbonyl stretching vibration bands, which do not coincide in the free ligand, merge into one absorption band in the complexes.

INTRODUCTION

In previous publications we described the syntheses and characterizations of coordination compounds of ketones, aldehydes, esters and amides as the ligands.[1–4] Only some of these ligands possess more than one carbonyl group, viz. dimethylphthalate[2] and diethyl malonate.[4] There are only very few other reports on coordination compounds with neutral bidentate oxygen-donor ligands, as for example diacetamide.[5] This is probably a consequence of the much poorer donor properties of such ligands compared to anionic bidentate oxygen-donor ligands and bidentate nitrogen-donor ligands. That the donor properties of the ligand under consideration are poor is illustrated by the impossibility to obtain complexes of N-acetylpyrrolidinone when starting from aquo-complexes, even when using dehydrating agents.[6] Only by utilizing the method of chloride-ion transfer we were successful in preparing metal(II)-solvates[7] of N-acetylpyrrolidinone. Hitherto no solvates nor adducts of N-acetylpyrrolidinone have been reported. This work is part of our investigations on the existence of coordination compounds of weak ligands.

EXPERIMENTAL

The ligand N-acetylpyrrolidinone was prepared by the method described by Tafel and Stern.[8] Nitromethane was used without further purification after storage over anhydrous calcium sulphate. Two methods were employed for the preparation of the complexes:[9] i) To a solution of 0.01 mol $[M(CH_3NO_2)_6](SbCl_6)_2$ in 20 ml nitromethane was added 0.03 mol N-acetylpyrrolidinone; ii) To 0.01 mol anhydrous MCl_2, 0.02 mol $SbCl_5.CH_3NO_2$ or 0.02 mol $InCl_3$, and 0.03 mol N-acetylpyrrolidinone in a thoroughly dried conical flask was added 20 ml nitromethane. In the case of nickel excess $NiCl_2$ (0.02 mol) was used. The various mixtures were stirred magnetically for three to twenty-four hours at room temperature. Non-reacted solid material was removed by filtration. The resulting clear solutions were concentrated by evaporation of the solvent in vacuo and were then allowed to crystallize. The solid compounds were collected on a glass filter and washed with sodium-dried n-pentane in a moisture-free atmosphere. Complexes of iron(II) and copper(II) could not be obtained. Attempts to prepare compounds $[M(NAP)_3](BF_4)_2$ with the aid of dehydrating agents from the corresponding hydrates[6] were not successful. Apparently the bidentate chelating ligand N-acetylpyrrolidinone is not strong enough to expel the ligand ethanol from the coordination sphere of the metal ion. The analytical and physical methods which were employed have been described previously.[2,7]

RESULTS AND DISCUSSION

In Table I seven new coordination compounds with 1-acetyl-2-pyrrolidinone as the ligand are listed with

TABLE I

Complexes of N-acetylpyrrolidinone (NAP), their analyses (% weight), melting points (°C), and colours

Compound	Metal(II)		Sb(V)/In(III)		Chloride		Melting Point	Colour
	calc.	found	calc.	found	calc.	found		
$Mg(NAP)_3(SbCl_6)_2$	2.26	2.23	22.7	22.4	39.6	39.4	203–205	white
$Mn(NAP)_3(SbCl_6)_2$	4.97	5.08	22.0	21.8	38.5	38.0	197 d.	white
$Co(NAP)_3(SbCl_6)_2$	5.31	5.42	22.0	22.2	38.4	38.6	140 d.	rosa-red
$Ni(NAP)_3(SbCl_6)_2$	5.29	5.13	22.0	21.6	38.4	37.8	145 d.	green
$Zn(NAP)_3(SbCl_6)_2$	5.86	5.76	21.8	21.9	38.1	37.9	87–88	white
$Co(NAP)_3(InCl_4)_2$	6.18	6.08	24.1	23.7	29.8	29.4	93–95	rosa-red
$Ni(NAP)_3(InCl_4)_2$	6.16	6.11	24.1	23.9	29.8	29.4	194–195	blue

d = decomposes

analytical data, colour and melting points. From the stoichiometry and the colour of the complexes a first indication is gained that the metal ions are hexacoordinated by the bidentate chelating ligands.

The presence of respectively the octahedral $SbCl_6^-$ anion and the tetrahedral $InCl_4^-$ anion is established by the occurrence of a strong absorption band at respectively about 345 cm^{-1} and about 330 cm^{-1} in the infrared spectra of the complexes (see Table II).[1-4,10,11]

Usually the interpretation of the infrared spectra of RR′C=O ligands and their complexes is quite straightforward.[1] In such compounds the carbonyl stretching vibration shifts to lower frequencies, whereby the magnitudes of the shifts are metal-dependent in the Irving–Willians order.[1,2] Similarly, the carbonyl bending vibration shifts to higher frequencies in the Irving–Williams sequence. With the N-acetylpyrrolidinone-solvates however it is not so simple: The infrared spectrum of the free ligand shows two carbonyl stretching vibrations. One at 1743 cm^{-1}, which has been assigned to the carbonyl group which is part of the ring and which has ketonic character, and one at 1697 cm^{-1} assigned to the

TABLE II

Infrared absorption bands (cm^{-1}) of N-acetylpyrrolidinone (NAP) and the compounds $M(NAP)_3(SbCl_6)_2$ and $M(NAP)_3(InCl_4)_2$.

NAP		Mg/Sb	Mn/Sb	Co/Sb	Ni/Sb	Zn/Sb	Co/In	Ni/In	
1743	s	1734	1736	1720	1723	1720	1723	1720	s
1697	s	–	–	–	–	–	–	–	
1296	vs	1311	1307	1307	1307	1304	1314	1308	s
1249 1232	d, m	1227	1223	1223	1224	1221	1229	1222	m
1196	m	1170	1170	1165	1163	1164	1165	1168	w
1130	m	–	–	–	–	–	–	–	
1044	sh	1038	1038	1037	1038	1037	1040	1038	d, m/w
1028	m	1024	1023	1024	1023	1023	1030	1026	
974	m	–	–	–	–	–	–	–	
933	m	947	947	950	949	948	950	951	m
892	w	896	895	895	896	896	895	894	w
846	m	843	844	846	849	847	844	846	w
718	vw	737	731	732	730	730	735	734	m
648	m	654	649	653	656	652	650	658	m
590	s	604	599	603	603	601	600	604	w
538	vw	550	547	562	570	555	560	573	w/m
–		478	479	481	486	480	480	486	m
394	w	431	413	423	427	424	426	426	m
		346	345	345	345	343	334	329	vs
		270	218	230	259	210	240	263	m

v = very, w = weak, m = medium, s = strong, sh = shoulder, d = doublet.

exocyclic amidic carbonyl group.[13] In the complexes of N-acetylpyrrolidinone these two carbonyl stretching vibration bands merge into one band. The positions of this band in the various complexes are not metal-dependent in the Irving–Williams sense and the band is rather broad. The explanation of this phenomenon may be as follows: In N-acetylpyrrolidinone itself the exocyclic carbonyl group and not the cyclic carbonyl group is of amidic character.[13] It is therefore clear that interaction exists between the nitrogen lone electron pair and the exocyclic carbonyl group. The cyclic carbonyl group does not interact with the nitrogen lone electron pair and therefore retains its ketonic character. When both carbonyl groups would have had interaction with the nitrogen lone electron pair, then both carbonyl groups would have had amidic character and only one carbonyl stretching vibration band – as with diacetamide – would have been observed, and, moreover, both carbonyl groups would have been in one plane. So in the case of the free ligand both carbonyl groups apparently are not in one plane. Upon bond formation to a metal ion through both oxygen atoms, however, both carbonyl groups will be forced into one plane, which means, incidentally, that a greater barrier towards complex-formation must be overcome then with other bidentate ligands. As a consequence, also, the carbonyl groups become more alike one another and their vibrations will thus differ less in frequency or will even merge together. Apparently the latter is the case (see Table II). The position of this 'fused' absorption band is rather high, from which one may conclude that the exocyclic carbonyl group loses its amidic character. That the Irving–Williams sequence is not observed could be a consequence of the strain which is put on the ligand by the metal ion and which levels out the differences in inductive effect of the metal ions on the ligand.

When the above argumentation holds, then also the conformation of N-acetylpyrrolidinone has become more rigid upon coordination. This is indeed the case, as can be inferred from the change in pattern of infrared absorption bands.[7,14,15] Compared to the infrared spectrum of the free ligand (see Table II) some bands (1130 cm^{-1}; 974 cm^{-1}) have disappeared, one band (around 480 cm^{-1}) has appeared, and some bands have changed in intensity (1296 cm^{-1}; 1196 cm^{-1}; 846 cm^{-1}, 718 cm^{-1}; 590 cm^{-1}) or in shape (1249/1232 cm^{-1}; 1028/1044 cm^{-1}). Between 200 cm^{-1} and 300 cm^{-1} (see Table II) one band appears in the infrared spectrum of each of the complexes, which is due neither to a ligand vibration, nor to an anion vibration. Its position is metal dependent in the Irving–Williams order,[12] and moreover, its position is highest in the Mg-complex. This band must be due to the species $\{M(\text{ligand})_3\}^{2+}$. Therefore we assign this band to the metal-oxygen stretching vibration.

The infrared spectra of the complexes are very similar to one another: The absorption bands lie in the same pattern and have the same relative intensities. This means that the solid compounds are largely isomorphous. The reflectance spectra of the cobalt and nickel compounds are typical for octahedral coordination. Accordingly (see Table III) assignments of the bands and calculations[16,17] of the ligand field parameters were performed. In Table IV values of the spectrochemical parameter Dq

TABLE III
Absorption bands (cm^{-1}) in the visible and near infrared, their assignments, and the calculated ligand field parameters of the cobalt and nickel compounds.

$Co(NAP)_3(SbCl_6)_2$	8550	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	Dq = 935 cm^{-1}
	15050	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	B = 810 cm^{-1}
	19600	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	Dq/B = 1.155
$Ni(NAP)_3(SbCl_6)_2$	9500	$^3T_{2g} \leftarrow {}^3A_{2g}$	Dq = 950 cm^{-1}
	13700 sh	$^1E_g \leftarrow {}^3A_{2g}$	Dq/B = 1.03
	15750	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	B = 0.89
$Co(NAP)_3(InCl_4)_2$	8750	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	Dq = 950 cm^{-1}
	19800	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	B = 815 cm^{-1}
			Dq/B = 1.165
$Ni(NAP)_3(InCl_4)_2$	9550	$^3T_{2g} \leftarrow {}^3A_{2g}$	Dq = 955 cm^{-1}
	13700 sh	$^1E_g \leftarrow {}^3A_{2g}$	B = 945 cm^{-1}
	15900	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	Dq/B = 1.01
	27200	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	

sh = shoulder.

TABLE IV
Values of the spectrochemical parameter Dq (cm^{-1}) for some cobalt and nickel complexes with oxygen donor ligands.[1,3,4,16-18]

	Co	Ni		Co	Ni
$[M(\text{ethylacetate})_6](SbCl_6)_2$	790	800	$[M(\text{diethylmalonate})_3](SbCl_6)_2$	905	910
$[M(\text{acetone})_6](InCl_4)_2$	860	860	$[M(2,4\text{-pentanedione})_3](ClO_4)_2$	–	975
$[M(\text{acetamide})_6](BF_4)_2$	880	865	$[M(\text{diacetamide})_3](ClO_4)_2$	965	950

for some monodentate and bidentate oxygen-donor ligands are listed: On going from the ester to the diester, and from the ketone to the diketone, and from the amide to the diamide the Dq-value increases significantly. This indicates that the ligand-field is more effective in the case of bidentate ligands, perhaps in consequence of shorter bonding distances. The Dq-values of N-acetylpyrrolidinone (see Table III) lie in the same range as the Dq-values of acetylacetone and diacetamide. So, on the basis of the Dq-values, it can not be decided whether the carbonyl groups of N-acetylpyrrolidinone have become ketonic or amidic in character upon complexing.

CONCLUSIONS

Only with the method of chloride-ion-transfer transition metal ion solvates of the neutral bidentate oxygen donor ligand N-acetylpyrrolidinone can be obtained.

The difference in character of the two carbonyl groups of N-acetylpyrrolidinone, one being amidic and one being ketonic, is equalized by bond formation to metal ions.

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