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The Coordination Chemistry of 2,6-Dimethyl-4-pyrone

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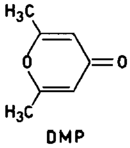
A number of new coordination compounds containing 2,6-dimethyl-4-pyrone (DMP) is reported. The compounds have the general formula $M(DMP)_nX_2$ with M = Mg, Mn, Co, Ni, Cu, Zn and Cd; n = 1, 2, 3, 4 or 6 and X = Cl, Br, BF_4, ClO_4 and NO_3. Contrary to earlier reports in which no adducts of $NiCl_2$ and $NiBr_2$ with DMP could be isolated, we now report $Ni(DMP)Cl_2$ and $Ni(DMP)_2Br_2$. The latter compound contains tetrahedrally coordinated Ni(II), which is highly unusual for this type of ligand. In the remaining compounds the metal ions are octahedrally coordinated, either by six DMP ligands (n = 6), or by both ligands and anions (n = 1, 4). No definite conclusions about the structure of $Co(NO_3)_2(DMP)_3$ are possible. With M = Cu and X = ClO_4, BF_4 two different compounds were obtained, viz. with n = 4 and n = 6. The compounds with n = 6 appear to contain two loosely bound DMP ligands. Conclusions about the structure of the compounds have been drawn with the aid of ligand-field spectra, infrared spectra, far–IR spectra, ESR spectra and X-ray powder diagrams. An assignment of the M–O stretching frequency has been made, which contradicts a previous one.

Introduction

Coordination compounds containing the ligand 2,6-dimethyl-4-pyrone (abbreviated DMP) are known for several years[1,2].



After an initial study by Gray[1] in which $CoCl_2(DMP)_2$, $MnCl_2(DMP)_2(H_2O)$ and $FeCl_2(DMP)_2(H_2O)$ were isolated, Briggs[2] reported several other compounds containing DMP, *i.e.*: $MX_2(DMP)_2$ with M = Co, Zn and X = Cl, Br, I all having a distorted tetrahedral geometry, $CuCl_2(DMP)$, $CuBr_2(DMP)_2$, $Ni(DMP)_6NiI_4$, $Cu(DMP)_4(ClO_4)_2$, $Cr(DMP)_6(ClO_4)_3$, $M(DMP)_6(ClO_4)_2$ with M = Co, Ni, Zn, $M(DMP)_2(NO_3)_2$ with M = Co, Ni, Zn, Cu; the latter compounds all have more or less distorted octahedral geometry.

Considering these earlier results, we observed a few pecularities, *i.e.*: a) no compounds with $NiCl_2$ and $NiBr_2$ could be isolated; b) the metal ions Mn(II) and Cd(II) are very poorly studied; c) with $Cu(ClO_4)_2$ no hexakis solvate was found, although they are known for several other oxygen-donor ligands[3–5]; d) with nitrates, only 2 mol of DMP are coordinated to the metal ions, despite the weakly coordinating tendencies of NO_3^-; e) the M–O stretching frequencies reported for the hexakis solvates are unusually high, compared with other C=O donor ligands[5–7].

This prompted us to a reinvestigation and extension of this system, which is described in the present paper. During the course of this investigation a few papers appeared describing some scandium compounds[8], *viz.* $Sc(DMP)_6X_2$ with X = ClO_4, Br, I, NCS, $Sc(DMP)_4X_3$, X = Cl, NO_3 and $Sc(DMP)_3(NCS)_3$, some rare-earth compounds[9–11], *viz.* $Ln(DMP)_8(ClO_4)_3$ (Ln = La, Nd, Sm), $Ln(DMP)_7(ClO_4)_3$ (Ln = Er, Eu, Gd, Yb), $Ln(DMP)_6(ClO_4)_3$ (Ln = La, Gd, Yb) and $LaCl_3(DMP)(H_2O)$. Further a congress paper reported $MCl_2(DMP)_n$ (n = 1, 2 and M = Mn, Cu) and also $NiCl_2(DMP)(H_2O)$[12].

Experimental

Syntheses

The ligand DMP was synthesised by standard procedures[13] from dehydroacetic acid and hydrochloric acid.

The coordination compounds were prepared by reaction of the metal salt (or its hydrate) with the stoichiometric amount of DMP, using ethanol, methanol or acetone as a solvent. In all cases triethyl orthoformate (EOF) or trimethyl orthoformate was used as a dehydrating agent[14]. For the preparation of the hexakis Cu(II) solvates a ratio 1:8 was used. For the syntheses of the halide compounds, several metal : ligand ratios were tried, but only one type of compound could be isolated. After filtration of the crystals, they were washed with dry diethyl ether and dried *in vacuo* (1 mm) at room temperature.

Analyses

The compounds were characterised by determination of the metal content (complexometric[15]). In addition carbon and hydrogen determinations were carried out.

Physical Methods

Infrared spectra of the compounds were obtained on an Infrascan Hilger and Watts instrument (4000–650 cm^{-1}) from Nujol mulls and KBr discs. Far-infrared spectra were recorded on a Beckman FIR 720 interferometer (400–50 cm^{-1}) as pressed discs in polythene.

Ligand-field spectra of the coloured compounds were performed on a Beckman DK-2 instrument (35,000–4000 cm^{-1}) by the diffuse reflectance technique.

X-ray powder patterns were obtained by the Guinier' method, using Cu-Kα radiation.

ESR spectra at X-band and Q-band frequencies were obtained on commercial Varian instruments as described elsewhere[16].

Results and Discussion

General

All new compounds are listed in Table I, together with their colours, melting points, analytical data and X-ray isomorphisms. A few compounds mentioned earlier, but studied in more detail in the present work, are also listed in Table I.

The compounds having less than four DMP molecules are sensitive to atmospheric moisture. The other compounds do not appear to be very hygroscopic.

In attempts to prepare an adduct of $NiCl_2$ in methanol, a compound of formula $NiCl_2(MeOH)(DMP)$ was first isolated. This compound loses MeOH upon heating *in vacuo*. It is remarked that earlier attempts[2] to prepare DMP compounds of $NiCl_2$ and $NiBr_2$ were unsuccessful. The fact that we were able to isolate the compounds may be due to the use of triethylorthoformate, which is a superior dehydrating agent. In this respect it is noted that the compound $Ni(DMP)_2Br_2$ could only be isolated in a pure state, when acetone was used as the solvent.

The use of this reagent may also be responsible for the isolation of $Cu(DMP)_6X_2$ ($X = ClO_4$, BF_4), compared with $Cu(DMP)_4(ClO_4)_2$ by Briggs[2]. However, attempts to prepare $M(DMP)_6(NO_3)_2$ were unsuccessful by this preparative method, although $Co(DMP)_3(NO_3)_2$ is different from Briggs' compound.

A few things should be mentioned about the isomorphisms and the melting points of the perchlorates and the tetrafluoroborates. In the first place it is observed that all hexakis solvates are isomorphous. This excludes the possibility of formulating $Cu(DMP)_6X_2$ as $[Cu(DMP)_4X_2](DMP)_2$; further evidence for real solvates $[Cu(DMP)_6]X_2$ comes from IR, UV, FIR and ESR data *(vide infra)*. Secondly, it is seen that for a given anion, the melting points follow the Irving–Williams sequence, Cd < Mn < Co < Ni > Zn. Thirdly, the tetrafluoroborate compounds have lower melting points than the corresponding isomorphous perchlorates, which is commonly observed[17, 18].

TABLE I. DMP Coordination Compounds, with Their Melting Points, Analytical Data, Colours, and Isomorphism.

Compound	Colour	Melting Point (° C)	Analytical Data						Isomorphism (Type)
			%M		%C		%H		
			Fnd.	Calc.	Fnd.	Calc.	Fnd.	Calc.	
$Mg(DMP)_6(ClO_4)_2$	White	213–4	2.60	2.51	51.8	52.1	4.7	5.0	A
$Mn(DMP)_6(ClO_4)_2$	White	210–3	5.54	5.50	50.5	50.5	5.0	4.9	A
$Co(DMP)_6(ClO_4)_2$	Violet[a]	223–4	5.90	5.88	50.1	50.3	4.8	4.8	A
$Ni(DMP)_6(ClO_4)_2$	Light Green[a]	244–6	5.80	5.86	49.9	50.3	5.1	4.8	A
$Cu(DMP)_6(ClO_4)_2$	Green	160–2	6.14	6.31	50.0	50.1	5.0	4.8	A
$Zn(DMP)_6(ClO_4)_2$	White[a]	180–1	6.41	6.48	50.0	50.0	4.9	4.8	A
$Cd(DMP)_6(ClO_4)_2$	White	210–5	10.6	10.6	47.6	47.8	4.4	4.3	A
$Cu(DMP)_4(ClO_4)_2$	Blue[a]	192–6	7.96	8.37	44.2	44.3	4.4	4.3	B
$Cu(DMP)_4(BF_4)_2$	Green–Blue	180–3	8.51	8.66	45.9	45.8	4.5	4.4	B
$Co(DMP)_6(BF_4)_2$	Violet	217–9	6.31	6.03	51.6	51.6	5.1	5.0	A
$Ni(DMP)_6(BF_4)_2$	Light Green	238–9	6.08	6.01	51.4	51.6	5.1	5.0	A
$Cu(DMP)_6(BF_4)_2$	Green	151–5	6.42	6.47	50.7	51.4	5.1	4.9	A
$Zn(DMP)_6(BF_4)_2$	White	176–9	7.10	6.64	50.8	51.3	5.0	4.9	A
$Mn(DMP)Cl_2$	White	>250	22.1	22.0	33.8	33.7	3.3	3.2	
$Cd(DMP)Cl_2$	White	>250	36.8	36.6	27.6	27.4	2.8	2.6	
$Ni(DMP)Cl_2$	Yellow	>250	23.9	23.1	29.8	33.1	3.2	3.2	
$Co(DMP)_3(NO_3)_2$	Purple	130–132	10.6	10.6	45.7	45.4	4.1	4.3	
$Ni(DMP)_2Br_2$	Deep Green	>250	11.8	12.6	37.0	36.0	3.6	3.4	

[a] Reported previously by Briggs[2].

Infrared Spectra

For a first characterisation of the solid products IR spectroscopy was used, to obtain information about: a) the possible presence of water or solvent molecules; b) the presence and possible coordination of complex anions (BF_4, ClO_4, NO_3); c) the occurrence of shifts in ligand vibrations (*e.g.* C=O stretching) upon coordination; d) the fine structure in the ligand vibrations for information about isomorphism.

Except for the methanol adduct of $Ni(DMP)Cl_2$ described above, none of the compounds showed the presence of vibrations other than those assigned to DMP and the anions.

It is however to be noted that most compounds (especially the halides) are more or less hygroscopic; therefore the compounds have to be stored in a dry atmosphere.

Variations due to the free anions are readily recognised in the compounds having complex anions[19]; *i.e.* bands at 1090 cm^{-1} (vs) and 620 cm^{-1} (s) for the perchlorates and bands at 1055 (vs) and 520 cm^{-1} (s) for the tetrafluoroborates. These bands are broadened in the compounds $Cu(DMP)_4X_2$ (X = ClO_4, BF_4), which can be ascribed to weak coordination of the anions, completing the distorted octahedron around Cu(II). This is further confirmed by the appearance of the "forbidden" symmetrical Cl–O stretching frequency at 920 cm^{-1} and the symmetrical B–F stretching frequency at 765 cm^{-1}.

The bands due to the nitrate anion in $Co(DMP)_3(NO_3)_2$, *i.e.* at 1450 (vbr, vs), 1025 (m) and 825 cm^{-1} (s), agree with literature values. Although the values indicate the occurrence of coordinated NO_3 ions, it cannot be concluded whether one or both of the anions are coordinated; also no conclusions are allowed from these data about monodentate or bidentate nitrate anions[19].

Since it is known that DMP coordinates to metal ions *via* the carbonyl oxygen[9,10], and since it is known that the C=O stretching frequency decreases upon coordination to metal ions, we have looked in more detail to the region in the IR where the C=O stretching frequency is to be expected, *viz.* 1700–1500 cm^{-1}. In this region at least three bands are observed, of which two shift to lower frequencies upon coordination. The band assigned to the C=O stretching is generally accepted to be the broad band at about 1540–1550 cm^{-1} [1,2]. Unfortunately, no Irving–Williams sequence of metal ions could be observed, due to the very broad bands, although the Cu(II) compounds showed the C=O stretching frequency at the lowest frequencies (1535 cm^{-1} against 1550–1555 for the other metal ions).

It was further observed that all compounds with the same X-ray powder pattern (Table I) showed very similar infrared spectra as regards to band shape and band splittings, indicating that these compounds are also infrared isomorphous. However, two compounds, *viz.* $Cu(DMP)_6X_2$ with X = ClO_4, BF_4, showed infrared spectra that are not isomorphous with the other hexakis solvates. Several ligand peaks appear to be split into two components. This effect has been observed previously[20,21] for some other oxygen-donor ligands, and must be due to a Jahn–Teller distortion of the Cu $(ligand)_6$ species. This distortion is not seen by the "slow" X-ray technique, but is clearly recognised by the "faster" infrared, ESR and UV (see below) techniques.

Ligand-field and ESR Spectra

For further characterisation of the coloured compounds containing unpaired *d* electrons, ligand-field spectra and ESR spectra (the latter only for Cu(II)) were recorded.

The spectral data are listed in Table II, together with some calculated parameters. The ligand-field spectra were only recorded in the solid phase because of possible ligand exchange in solution. The values for $Ni(DMP)_6X_2$ are close to those reported by Briggs[2] and agree with octahedral geometry. The same holds for $Co(DMP)_6X_2$. The differences between the perchlorates and the tetrafluoroborates are within experimental error and are in agreement with the same geometry for both compounds. The calculated Dq and B values for these compounds can be compared with other ligands in the spectrochemical series[17,20,22,23,24]. It is then observed that DMP is a moderately strong C=O donor ligand compared with other C=O donor ligands[24]. In fact the parameters are intermediate between acetone and acetophenone.

The observed band maxima for $Ni(DMP)Cl_2$ also agree with octahedral geometry for the cation. The calculated parameters are close to those of $NiCl_2$[22], in agreement with a supposed coordination polyhedron built up by ($NiCl_5O$).

The band maxima for $Ni(DMP)_2Br_2$, on the other hand, agree with tetrahedral geometry for the cation. This geometry is highly unusual for C=O donor ligands; in most cases species $NiBr_2L_2$ of tetrahedral geometry are formed only with bulky ligands, like phosphines and sterically hindered amines. No attempts were undertaken to calculate Dq and B values for this compound, because of the very low symmetry caused by the different nature of the ligands.

Also for $Co(DMP)_3(NO_3)_2$ no ligand-field parameters can be calculated, although the band maxima might be interpreted on an octahedral basis. However, tetrahedral geometry might also be possible. A distorted geometry has been observed previously[25,26] for other compounds of $Co(NO_3)_2$.

The observed ligand-field and ESR spectra and calculated parameters for the compounds $Cu(DMP)_4X_2$ agree with a square planar geometry for Cu(II), with weakly coordinating anions[27]. The slightly higher

TABLE II. Ligand-field and ESR Spectra of DMP Coordination Compounds, with Calculated Parameters.

Compounds	Ligand-field Maxima (in kK)	Ligand-field Parameters (in cm^{-1})		
		Dq	B	
$Ni(DMP)_6(ClO_4)_2$	8.25^a 13.4 14.4 24.4	825^{a,b}	900^{a,b}	
$Ni(DMP)_6(BF_4)_2$	8.25 13.5 14.3 24.4	825	900	
$Co(DMP)_6(ClO_4)_2$	7.6 18.8 20.8 sh	830	840	
$Co(DMP)_6(BF_4)_2$	7.6 18.7 20.8 sh	830	840	
$Ni(DMP)Cl_2$	7.2 11.4 12.8 sh 22.0	720	800	
$Ni(DMP)_2Br_2$	4.0 vbr,w 6.65 12.5 14.5 sh 16.2			
$Co(DMP)_3(NO_3)_2$	8.3 11.6 sh 18.7 br			
		ESR Parameters^{c,d}		
		$g_\perp$	$g_\parallel$	$A_\parallel$
$Cu(DMP)_4(ClO_4)_2$	14.8	2.07	2.35	143
$Cu(DMP)_4(BF_4)_2$	14.7	2.07	2.35	145
$Cu(DMP)_6(ClO_4)_2$	12.5 9.5 w,sh	2.07	2.37	95
$Cu(DMP)_6(BF_4)_2$	12.0 9.3 w,sh	2.06	2.38	107

[a] Ligand-field maxima are accurate to 0.1 kK; parameters are accurate to 10 cm^{-1}. [b] Ligand-field parameters are calculated according to ref. 22 and 25. [c] A values are expressed in Gauss. [d] g values are accurate to 0.01; A values are accurate to 5 Gauss.

energy of the L.F. maxima for X = ClO_4 might be due to a relatively stronger bonding of the equatorial ligands. Both ESR and L.F. spectral data for the compounds $Cu(DMP)_6X_2$ agree with a species $Cu(DMP)_6$ which is distorted by a Jahn–Teller mechanism. The differences in spectral parameters between the two classes of compounds exclude the possibility of a species $[Cu(DMP)_4X_2](DMP)_2$ for the latter class of compounds. We will return to this problem below, in the discussion of the far-infrared spectra.

Far-infrared Spectra

Finally, far-infrared spectra of the compounds were studied to obtain insight into the strength of the metal–ligand bond. Spectral data for the region 400–50 cm^{-1} are listed in Table III.

Some tentative assignments are also indicated in this Table. These assignments are completely different from a previous one. Briggs *et al.*[2] assigned a band around 370 cm^{-1} to the metal–ligand stretching frequency. Inspection of our Table shows several arguments for disagreement with the assignment of this band to a M–O stretching: i) The nearly equal frequency for the Mn(II) and Cd(II) compounds, despite of their large difference in mass. ii) The low value of the so-called M–O stretch for the Mg(II) compound. In all known series of compounds with a particular ligand, the Mg(II) compound has the highest M–O stretching frequency. Moreover, all other known compounds with a C=O donor ligand have M–O stretching frequencies of a much lower energy[16, 17, 19].

A more likely candidate for the M–O stretching frequency is the absorption varying from 217 cm^{-1} (Cd) to 304 cm^{-1} (Mg). The sequence of metal ions, according to increasing frequency, very nicely follows known effects based upon mass differences and the Irving–Williams series.

A second far-infrared absorption, which is strongly dependent upon the metal ion is observed in the region 161 (Cd) to 242 (Cu) cm^{-1}. This absorption can be assigned to a M–L bending or wagging vibration[19]. Sometimes, this absorption appears as a split band, probably due to mixing with a ligand band near 190 cm^{-1}.

A few further remarks with respect to the values listed in Table III can be made. In the first place the ligand vibration at 360–390 cm^{-1} (arising from the free ligand band at 335 cm^{-1}) beautifully follows the Irving–Williams sequence of metal ions, *i.e.* Mn < Co < Ni < Cu > Zn. Secondly, in case of the hexakis Cu(II) solvates, this absorption is split into two components. It seems likely that these two components arise from four strongly bound ligands (strong band at 390, resp. 395 cm^{-1}) and two rather weakly bound ligands (medium intense band at 352, resp. 346 cm^{-1}). The difference between the perchlorate and the tetrafluoroborate which is beyond the experimental error, agrees with the picture obtained from the ligand-field spectra, which showed the largest distortion for the perchlorate (*i.e.* the strongest bonding in the equatorial plane and the weakest bonding in the axial direction). Thirdly, it is seen that the other ligand vibrations (below 300 cm^{-1}) are hardly dependent upon the metal ion. In a few cases there is considerable overlap or mixing with a metal–ligand vibration around 200 cm^{-1}.

TABLE III. Far-infrared Spectra (400–50 cm^{-1}) of Coordination Compounds Containing DMP, and Tentative Assignments.

Compound	Ligand Absorptions				M–O Stretches	Other M–L Vibrations	M–X Stretch	Unassigned
DMP	335 m	280 w	190 w	82 w 71 w				
$Cd(DMP)_6(ClO_4)_2$	360 s	283 m	190 sh	94 w 83 w	217 s	203 sh, 161 m		
$Mn(DMP)_6(ClO_4)_2$	361 vs	285 s	194 sh	78 m,br	235 vs	204 vs		132 w, 110 w
$Zn(DMP)_6(ClO_4)_2$	368 vs	284 s		80 w,br	234 vs	193 s, 180 s		141 m
$Zn(DMP)_6(BF_4)_2$	368 vs	284 s		80 w,br	233 vs	194 s, 180 s		143 m
$Co(DMP)_6(BF_4)_2$	371 vs	285 s	197 m	77 m,br	250 vs	212 vs		153 vw
$Co(DMP)_6(ClO_4)_2$	370 vs	284 s	190 sh	79 m	248 vs	210 vs		143 w, 119 w
$Ni(DMP)_6(ClO_4)_2$	378 vs	285 s	187 sh	80 s,br	263 vs	225 s,br		150 vw
$Ni(DMP)_6(BF_4)_2$	378 vs	285 s	195 sh	77 s,br	264 vs	226 s,br		150 vw
$Cu(DMP)_6(BF_4)_2$	390 s, 352 m	288 s	192 sh	79 m	269 s	231 s, 212 s, 203 s		155 m
$Cu(DMP)_6(ClO_4)_2$	395 s, 346 m	292 s	190 m	80 m	271 vs	242 s, 228 s, 220 m, 207 m		153 s, 114 w
$Mg(DMP)_6(ClO_4)_2$	367 vs	285 sh	185 sh	78 m,br	304 vs	223 m, 201 m		145 w, 120 w
$Cu(DMP)_4(ClO_4)_2$	398 vs	291 s		86 s,br	268 vs	231 w, 204 s		159 m
$Cu(DMP)_4(BF_4)_2$	399 vs	290 s		90 s,br	268 vs	228 w, 204 s		158 m
$Ni(DMP)_2Br_2$	374 s	281 s	197 m	68 m,br	258 vs		221 vs	181 w, 162 w
$Ni(DMP)Cl_2$	378 s	280 s	197 m	75 w,br	255 sh, 245 s	227 s	218 s, 208 s	151 m
$Mn(DMP)Cl_2$	365 s	284 s		75 w	265 s, 245 s		210 vs,vbr	122 s, 90 w
$Cd(DMP)Cl_2$	363 m	285 m		72 m	210 s	164 s	190 s, 110 s	
$Co(DMP)_3(NO_3)_2$	370 s	285 vs	190 sh	85 w,br	240–200 vs,vbr		295 s,sh	145 vw, 132 w

No attempts were undertaken for a detailed assignment of the bands below 200 cm^{-1}.

The assignments in the metal–halide compounds are based upon the findings with the hexakis solvates. The very strong band at 221 cm^{-1} for $Ni(DMP)_2Br_2$ agrees with a tetrahedrally coordinated cation[19, 28]. The metal–halogen stretches for the polymeric metal–chloride adducts are also in the usual region[28]. No new conclusions can be drawn from the band maxima of $Co(DMP)_3(NO_3)_2$.

Conclusion

From the results of the present investigation, the following conclusions can be drawn:

1. Metal(II) perchlorates and tetrafluoroborates form an isomorphous series of coordination compounds with the ligand 2,6-dimethyl-4-pyrone of formula $M(DMP)_6X_2$, with M = Mg, Mn, Co, Ni, Zn, Cd and Cu.

2. Contrary to earlier reports, hexakis solvates can also be prepared for M = Cu(II). The octahedral coordination around the Cu(II) ion is tetragonally distorted, however, as concluded from infrared, ligand-field, ESR and far-IR spectra.

3. Contrary to earlier reports adducts of $NiCl_2$ and $NiBr_2$ could be synthesised; this is probably due to the use of triethyl orthoformate as a dehydrating agent. The structure of the compound $Ni(DMP)_2Br_2$ is built up with tetrahedrally coordinated Ni(II) ions.

A compound $Co(DMP)_3(NO_3)_2$ for which no definite structure has been proposed, was also isolated, compared with $Co(DMP)_2(NO_3)_2$ in a previous study. No hexakis solvates with metal nitrates could be prepared.

4. For the octahedrally coordinated metal(II) solvates the M–O stretching frequency occurs in the 215–305 cm^{-1} region (from Cd–Mg), which falls in the region usually observed for C=O donor ligands. This assignment contradicts an earlier far-IR investigation on some of these compounds.

5. The ligand-field strength of DMP is moderately large compared with other C=O donor ligands. No direct influence is seen on the ligand-field parameters of the double bonds in the ring system or by the electronic effect of the oxygen in position 4.

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