Contribution from the Department of Inorganic Chemistry,
State University, P.O. Box 75 Leyden, The Netherlands

Complexes with Ligands Containing Nitrile Groups. XV.[1]
The Ligand Properties of Benzylcyanide

C. D. Jansen-Ligthelm, W. L. Groeneveld and J. Reedijk*

Received April 29, 1972

A number of solvates with general formula $M(L)_n(anion)_2$ is reported, in which L stands for benzylcyanide. The cations are the divalent ions of Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd; n is 6 in most cases except for one Cu compound (n = 4) and one Co compound (with n = 7). The anions used are $SbCl_6^-$, $InCl_4^-$, and $FeCl_4^-$. No pure compounds with the BF_4^- anion could be obtained.

Physical measurements such as infrared spectra, ligandfield spectra, EPR spectra and Mössbauer spectra indicate regular octahedrons $M(benzylcyanide)_6^{2+}$ for all compounds, except those of Cu^{II}. The ligandfield strength of benzylcyanide is close to that of CH_3CN and C_6H_5CN.

Introduction

Previous papers in the present series dealt with complexes containing acetonitrile[1-3], benzonitrile[4] and substituted benzonitriles.[5] A study concerning cloroacetonitriles is in progress.[6]

These former investigations have shown that electronic influences of substituents in the CN group are less important for the formation and properties of the complexes, than steric influences. Those steric influences, however, are rather small for benzonitrile and substituted benzonitriles, because these molecules contain substituents placed symmetrically on the CN group.

We now extended this study to a non-linear ligand, *i.e.* a ligand with a substituent placed asymmetric upon the CN group, in order to see the effect upon stoichiometry and geometry of the formed complexes.

For that purpose coordination compounds $[M(benzylcyanide)_6](anion)_2$ were prepared. As anions the large chloroanions MCl_n^- were chosen, that are known to show weak tendencies to take part in the coordination.

Experimental Part. As most of the compounds were very sensitive to hydrolysis, the synthesis and all handling operations were carried out in a P_2O_5-dried glove box, or in a cold (–5°) laboratory room.

Starting materials. Nitromethane was used as a solvent after drying over anhydrous calcium sulfate. Antimony pentachloride was used without further purification, and handled as the adduct $SbCl_5(CH_3NO_2)$ previously described by *Driessen.*[7] The metal chlorides were prepared by dehydrating the commercial hydrates *in vacuo* at 150°C, except for the chlorides of Fe^{II}, Fe^{III}, Zn^{II}, Cd^{II} and In^{III}, which were prepared as described in the literature.[8] The ligand was commercially available, used without further purification and kept in molecular sieves-4A.

Preparation of the solvates. The complexes with the chloroanions were synthesized by stirring each of the divalent metal halides (about 1.3 g.) with the chloro-acceptor MCl_n in a ratio 1 : 2 for about 24 hours in nitromethane (20-25 ml). Remaining parts of the metal halides were removed centrifugally. In this way a bright solution of nitromethane solvate was obtained. The coordinated nitromethane was replaced by the ligand after adding 6 moles of benzylcyanide.

The coordination compounds with the $SbCl_5^-$ anions thus prepared separated within a few hours standing in the cold (0-5°C.), and were isolated by filtration and dried *in vacuo* at room temperature.

The compounds with the $FeCl_4^-$ anions needed the addition of pentane and standing in the cold for crystallization.

Complexes with BF_4 anions were tried to prepare via the acetic acid solvates.[9] Only with Co and Ni^{II} tetrafluoroborates solid complexes could be obtained under these circumstances, that appeared to be extremely hygroscopic. Despite of precautions to exclude moisture, these latter compounds show OH absorptions near 3500 cm^{-1} in their infrared spectra. Therefore no further measurements were carried out with fluoroborates.

Analyses. The divalent metals, Fe^{III} and In^{III} were determined by complexometric titration as described

---

* Address for correspondence: Dr. J. Reedijk, Department of Chemistry, Technological University, Julianalaan 136, Delft, The Netherlands.

(1) Part XIV. G. Brokaar, W.L. Groeneveld, and J. Reedijk, *Rec. Trav. Chim.*, *89*, 1117 (1970).

(2) A.P. Zuur and W.L. Groeneveld, *ibid.*, *86*, 1089 (1967).

(3) J. Reedijk and W.L. Groeneveld, *ibid.*, *87*, 513 (1968).

(4) A.P. Zuur, A.H.L. Reintjes, and W.L. Groeneveld, *ibid.*, *89*, 385 (1970).

(5) C.A.A. van Driel and W.L. Groeneveld, *ibid.*, *90*, 389 (1971).

(6) H.P. Zoetmulder and W.L. Groeneveld, to be published.

(7) W.L. Driessen and W.L. Groeneveld, *Rec. Trav. Chim.*, *88*, 491 (1969).

(8) G. Brauer, Handbuch der Preparativen Anorganische Chemie, F. Enke Verlag, Stuttgart, 1962.

(9) P.W.N.M. van Leeuwen, *Rec. Trav. Chim.*, *87*, 396 (1968).

(10) G. Schwarzenbach. Die komplexometrische Titration, F. Enke Verlag, Stuttgart, 1965.

Table I. Benzylcyanide complexes, analyses, colours, X-ray types and melting points.

Compound	Calculated analyses			Found analyses			Colour	X-ray type	melting point(C)
	%M	%Cl	%M'	%M	%Cl	%M'			
$Mg(L)_6(SbCl_6)_2$	1.74	30.47	17.44	1.70	28.96	—	white	A	[a]
$Mn(L)_6(SbCl_6)_2$	3.85	29.84	17.08	3.12	28.59	16.78	yellow	A	145
$Fe(L)_6(SbCl_6)_2$	3.91	29.80	17.05	—	28.59	16.88	yellow	A	150
$Co(L)_6(SbCl_6)_2$	4.12	29.76	17.03	3.98	28.93	16.54	orange	A	95 dec.
$Ni(L)_6(SbCl_6)_2$	4.10	29.76	17.03	3.86	28.43	16.49	blue	A	170
$Cu(L)_6(SbCl_6)_2$	4.43	29.66	16.96	—	29.79	—	green	A	85 dec.
$Zn(L)_6(SbCl_6)_2$	4.55	29.60	16.94	4.23	29.26	16.75	cream	A	110
$Cd(L)_6(SbCl_6)_2$	7.57	28.66	16.41	—	28.59	16.78	cream	A	[a]
$Mg(L)_6(FeCl_4)_2$	2.17	25.27	9.95	—	22.42	10.51	cream	B	80
$Mn(L)_6(FeCl_4)_2$	4.76	24.60	9.69	4.94	24.48	10.04	red-brown	B	80
$Fe(L)_6(FeCl_4)_2$	4.84	24.58	9.68	4.86	24.43	9.72	green-brown	B	90
$Co(L)_6(FeCl_4)_2$	5.09	24.51	9.65	5.19	25.77	10.38	red-brown	B	95
$Ni(L)_6(FeCl_4)_2$	5.07	24.52	9.65	5.26	25.5	10.52	green	B	85
$Cu(L)_4(FeCl_4)_2$	6.85	30.58	12.04	6.58	26.77	11.57	green	—	98
$Zn(L)_6(FeCl_4)_2$	5.62	24.38	9.60	5.90	24.26	10.07	red-brown	B	75
$Cd(L)_6(FeCl_4)_2$	9.28	23.43	9.23	8.76	23.96	8.79	brown	B	75
$Mn(L)_6(InCl_4)_2$	4.32	22.31	18.06	4.18	21.50	17.45	yellow	D	65
$Co(L)_6(InCl_4)_2 . L$	4.22	20.37	16.49	4.02	20.58	16.68	orange	—	60
$Ni(L)_6(InCl_4)_2$	4.60	22.25	18.01	4.54	22.51	17.76	blue	D	75

[a] Very hygroscopic

Table II. CN stretching frequencies of benzylcyanide compounds, compared with liquid benzylcyanide (2250 cm^{-1}) ± 5 cm^{-1}

Cations	Anions:	$SbCl_6^-$	$FeCl_4^-$	$InCl_4^-$
Mg		2270w, 2300 [a]	2260w, 2290 [a]	—
Mn		2280	2280	2280
Fe		2290	2280	—
Co		2290	2295	2290, 2250 [b]
Ni		2300	2300	2300
Cu		2270, 2305 [c]	2320	—
Zn		2290	2295	
Cd		2285	2270w, 2290	—

[a] The weak bands are due to hydrolysis during mulling; [b] The band at 2250 cm^{-1} is due to uncoordinated ligand; [c] Doublet due to Jahn-Teller distortion [2,3].

by Schwarzenbach.[10] The metal analysis in the Cu/Sb compound was hampered by the Sb presence. Chlorine was determined by Volhard's method. Antimony was titrated iodometrically as described by Vogel.[11]

Measurements. Infrared spectra (4000-400 cm^{-1}) were obtained with a Unicam SP-1200 instrument as nujol mulls sandwiched between NaCl plates. The spectra in the far-IR region (700-50 cm^{-1}) were performed with a Grubb-Parsons Cube MK-2 interferometer and a Hitachi EPI-L spectrophotometer.

Ligand-field spectra were recorded by the diffuse reflectance method on a Beckman DK-2A instrument using MgO as a reference. X-ray powder diagrams were obtained by the Guinier method. The compounds were mounted with vaseline and protected from the atmosphere by adhesive tape.

Paramagnetic Resonance Spectra were recorded on Varian instruments at both X- and Q-band frequencies, as described elsewhere.[12]

A Mössbauer spectrum of $Fe(L)_6(SbCl_6)_2$ was obtained with a constant acceleration spectrometer as described by van der Kraan and de Blois,[13] furnished with a 25 mC^{57}Co source diffused into a 10 μm Pd foil. The measurement was carried out at 90°K.

Results and Discussion

The new compounds are listed in Table I together with their analytical data, colours, X-ray types and melting points. Several of these compounds were found to have mutually similar X-ray powder diagrams types A, B, and C in Table I), strongly suggesting the same metal-ion environments and packings in these compounds.

Of the $SbCl_6^-$ compounds $Co(L)_6(SbCl_6)_2$ decomposed very rapidly upon heating and even upon standing at room temperature for some days. The compound $Mg(L)_6(FeCl_4)_2$ could not be obtained pure, although its X-ray powder pattern demonstrated its presence.

Despite of many attempts, only Co, Ni and Mn compounds could be obtained with the $InCl_4^-$ anion. From these $Co(L)_6(InCl_4)_2$ appeared to contain an extra molecule benzylcyanide in the lattice, just as found for some acetonitrile compounds.[2,3]

Infrared Spectra in the CN Stretching Region. As demonstrated by Purcell,[14] all nitriles coordinated to

---

(11) A.I. Vogel, A. textbook of Quantitative Inorganic Analysis, Longmans, London, 1964.

(12) R.D. Dowsing, B. Nieuwenhuijse, and J. Reedijk, *Inorg. Chim. Acta*, *5*, 301 (1971).

(13) A.M. van der Kraan and J. de Blois, *Reactor Instituut, Delft, Rept.*, 132-68-01.

Table III. Ligand-field maxima (kK) of benzylcyanide compounds assignments and calculated parameters (cm^{-1}).

Compounds	Maxima with assignments				Parameters Dq	B
	$^5E_g \leftarrow {}^5T_{2g}$					
$Fe(L)_6(SbCl_6)_2$	11.2	9.5 sh			1120	
$Fe(L)_6(FeCl_4)_2$	[a]	10.8			1080	
		$^2P, {}^4T_{1g}(P) {}^4A_{2g} \leftarrow$		$^4T_{2g} \leftarrow {}^4T_{1g}(F)$		
$Co(L)_6(SbCl_6)_2$		20.7		9.5	1040	835
$Co(L)_6(InCl_4)_2 . L$		[a]		9.5	1040	
$Co(L)_6(InCl_4)_2 . L$		20.8		9.5	1045	840
	$^3T_{1g}(P) \leftarrow$	$^3T_{1g}(F) \leftarrow$	$^1E_g \leftarrow$	$^3T_{2g} \leftarrow {}^3A_{2g}$		
$Ni(L)_6(SbCl_6)_2$	[b]	17.5	13.3 w	10.8	1080	890
$Ni(L)_6(FeCl_4)_2$	[a]	[a]	13.2 w	10.85	1085	
	28.2	17.6	13.3	10.8	1080	885
			$^2T_{2g}, {}^2A_{1g} \leftarrow {}^2B_{1g}$			
$Cu(L)_6(SbCl_6)_2$			13.1	10.0 sh	1310	
$Cu(L)_4(FeCl_4)_2$			14.6		1460	

[a] Masked by $FeCl_4^-$ absorptions[3]. [b] Masked by $SbCl_6^-$ absorptions. [c] Bandmaxima are accurate to 0.1 kK; parameters are accurate to 5-10 cm^{-1}.

Table IV. EPR and Mössbauer parameters of benzylcyanide complexes.

Compound	EPR: g-value	D [a]	λ	Mössbauer: [b] C.S.(90K)	ΔE_q
$Fe(L)_6(SbCl_6)_2$	—	—	—	1.50	0.39
$Ni(L)_6(SbCl_6)_2$	2.190	0.27	0.02		
$Ni(L)_6(SbCl_6)_2$	2.180	0.14	0.02		

[a] D values (cm^{-1}) are accurate to 0.01; g values are accurate to 0.005; λ is accurate to 0.01. [b] Mössbauer parameters are in mm/s with respect to sodium nitroprusside and are accurate to ± 0.03 mm/s.

Lewis-acids should show an increase in the C≡N stretching frequency, due to an increase in the CN force constant. This has been confirmed by previous work[15] from this laboratory. Recently[16] it was shown that nitriles coordinated to π-donor metal ions (such as Ru^{2+}) have decreased C≡N stretching frequencies.

Our present compounds show the normal behaviour in their infrared spectra, with increased C≡N stretching frequencies. The value for the several compounds are listed in Table II, and are compared with ν_{CN} of the free ligand. It is observed that within an isomorphous series of compounds the Irving-Williams sequence of metal ions holds with respect to the position of the C≡N stretching.

The other vibrations of benzylcyanide remain unshifted upon coordination and will not be discussed in detail. In the far-infrared region, the compounds show very strong anion vibrations (at 375 cm^{-1} for $FeCl_4$, at 335 cm^{-1} for the $SbCl_6$ and $InCl_4$ anions[17]). Due to the rather bad mulling properties of the compounds, no intense metal-ligand vibrations could be determined in the region 300-50 cm^{-1}. It is planned to repeat these measurements later at temperatures as low as liquid nitrogen, where most coordination compounds yield much better resolved far-infrared spectra.

Ligand-field Spectra. For further information about the geometry of the ions $M(ligand)_6^{2+}$ ligand-field spectra of the coloured ones were recorded in the 2000-325 nm region. Band-maxima assignments and calculated parameters are presented in Table III. Ligand-field parameters for the cobalt and nickel compounds were calculated by standard procedures. For the Fe and Cu compounds the band maximum was taken to be equal to 10 Dq. Comparison with previous work on acetonitrile[1-3] and benzonitrile,[4] shows that benzylcyanide is a somewhat stronger ligand than benzonitrile and of the same strength as acetonitrile. In addition the spectra do not show large deviations from octahedral geometry for the species $M(L)_6$, just as found from the infrared spectra where one single CN stretching frequency was found.

EPR and Mössbauer measurements. The measurements discussed above, only gave rough information about the coordination around metal ions and no details about possible small distortions of the octahedron $M(L)_6$ can be derived from them.

Therefore, some suitable compounds were studied further with the aid of Mössbauer spectroscopy and Electron Paramagnetic Resonance Spectroscopy, since these techniques may yield detailed information about the first coordination sphere around metal ions.

The compounds chosen are $Fe(L)_6(SbCl_6)_2$ (for a Mössbauer spectrum) and $Ni(L)_6^{2+}$ $(anion)_2^-$, with $SbCl_6^-$ and $InCl_4^-$ anions (for EPR spectra). The results of the measurements are listed in Table IV. The Mössbauer isomer shift for $Fe(L)_6(SbCl_6)_2$ is close

---

(14) K.F. Purcell, *J. Am. Chem. Soc.*, *89*, 247 (1967).
(15) J. Reedijk, A.P. Zuur, and W.L. Groeneveld, *Rec. Trav. Chim.*, *86*, 1127 (1967).
(16) P.C. Ford and R.E. Clarke, *Chem. Commun.*, 1968, 1109.
(17) J. Reedijk and W.L. Groeneveld, *Rec. Trav. Chim.*, *87*, 1079 (1968).

to that reported for the species $Fe(CH_3CN)_6^{2+}$ (1.49-1.54 mm/s)[3,18] and for the species $Fe(benzonitrile)_6^{2+}$ (1.48 mm/s).[18] This indicates the same kind of metal-ligand bonding in the species $Fe(L)_6^{2+}$, and agrees with the results obtained from the ligand-field spectral parameters.

The value for the quadrupole splitting, ΔE_q, is very small, indicating a hardly distorted octahedron $Fe(benzylcyanide)_6^{2+}$; similar regular octahedrons are found for $Fe(CH_3CN)_6^{2+}$ with MCl_4^- anions,[18,19] although distorted octahedral species $Fe(nitrile)_6^{2+}$ also occur[3,18,19] (ΔE_q values up to 3 mm/s).

Similar regular octahedral groups can be derived from the EPR parameters of the Ni^{II} compounds. The small D-values of about 0.2 cm^{-1} are indicative for octahedral Ni^{II} with a small axial distortion.[20,21] The observed g-value is in the usual region for Ni^{II} coordinated by six nitrogen-donor ligands.[21]

Conclusion

From the above results the following conclusions can be drawn:

1) Benzylcyanide behaves as a normal *N*-donor nitrile with respect to coordination with divalent metal ions.

2) The octahedral groups $M(benzylcyanide)_6^{2+}$ are hardly distorted by axial or rhombic fields, despite of the asymmetric geometry of the ligand.

3) The position of benzylcyanide in the spectrochemical and nephelauxetic series is close to that of acetonitrile and slightly above benzonitrile.

Acknowledgement. The authors are indebted to Mr. J. van der Linde for assistance with the infrared spectra, to Mr. J.A. Smit for help with the analyses and X-ray powder measurements, to Mr. A. Vermaas and Dr. A.M. van der Kraan for recording the Mössbauer spectrum, and to Mr. P.G. van den Akker, Drs. B. Nieuwenhuyse and Mr. Vos for the performance of the EPR spectra.

(18) G.M. Bancroft, M.J. Mays, and B.E. Prater, *Chem. Phys. Letters, 4,* 248 (1969).
(19) J. Reedijk, Thesis, Leyden, 1968.
(20) C.J. Ballhausen, Introduction to Ligand Field Theory, Mc Graw Hill, London, 1962.
(21) J. Reedijk and B. Nieuwenhuijse, *Rec. Trav. Chim., 91,* 533 (1972).