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The Coordination Chemistry of Carbonyl Compounds

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The solvating properties of a number of carbonyl compounds have been investigated. The ligands used are acetaldehyde, propionaldehyde, benzaldehyde, methylformate, formamide, N,N-dimethylformamide, acetone, chloroacetone, butanone, acetophenone, ethylacetate, acetamide, N,N-dimethylacetamide, acetanilide, chloroacetamide, trimethylacetamide, benzamide, nicotineamide, 2-nitrobenzamide, 2,6-dichlorobenzamide, urethane, urea and dimethylcarbamoylchloride.

The complexes are characterized and identified by means of chemical analysis and physical measurements. Ligand-field parameters are reported for the solvates of cobalt(II) (in the solid state) and nickel(II) (both in the solid state and in nitromethane solution).

A (linear) correlation between the ligand-field parameters and parameters describing certain electronic effects of the substituents R_1 and R_2 in R_1R_2CO molecules, has been investigated; it is shown that no correlation exists.

Introduction

Complexes containing carbonyl compounds (general formula R_1R_2CO) as ligands were prepared as early as in 1901.[1] In following years quite a number of carbonyl complexes have been prepared and identified; in fact, the number of complexes now known is so large that it is impossible to review here in detail all investigations on this subject.

However, we will mention a few investigations pertinent to this work: Drago *et al.*[2,3] prepared and identified a series of amide complexes towards Ni^{II} and Cr^{III}. These studies were undertaken to investigate a correlation between the ligand-field parameters Dq and β and the enthalpy of adduct formation between the ligands and phenol or iodine.[4,5] Because this was the first systematic investigation of substituent effects on ligand-field parameters, these studies are rather important. As regards the results (which were quite remarkable), we can best cite Drago:[6] "For a series of amides of the type $R_1C(O)N(R_2)R_3$ it was found that whenever R_1 and R_2 are both alkyl groups, lower values for Dq and β result for the six coordinate nickel complexes than when either R_1 or both R_2 and R_3 are hydrogens. This is not in agreement with the observation that toward phenol and iodine the donor strengths of these amides are found to increase with the number of alkyl groups. It was proposed that a steric effect exists between neighbouring coordinated amide molecules in the metal complexes".

Although the enthalpy investigations were extended to carbonyl ligands other than amides[7,8] and acceptors other than phenol or iodine,[8] the ligand-field parameters investigations remained restricted to amide complexes.[9,10] Most probably this was caused by synthetic problems.

Recently, we studied the coordination chemistry of phosphoryl compounds.[11,12] It was shown that the ligand-field parameters did not vary significantly with the substituents investigated.[11,12] It seemed therefore interesting to extend the investigation to other oxygen-donor ligands, in order to see whether or not such behaviour is typical for oxygen-donor complexes.

Now Driessen[13,14] recently discovered a new procedure for the preparation of a certain type of complexes (those of "weakly coordinating oxygen-donor ligands"). Quite a few of the new complexes that he prepared were carbonyl complexes which could hitherto not be synthesized.

Because of these reasons, an investigation of the possible existence of a correlation between ligand-field parameters of carbonyl complexes and substituent group electronic parameters, has been undertaken by us.

The present paper is divided in two sections. The first section deals with the preparation and identification of a number of new carbonyl complexes. The second section deals with the investigation of the correlation mentioned above.

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Experimental Section

Starting materials. Most metal salts were commercially available or were prepared by standard procedures.[15] The ligands were all commercially available and were used without further purification.

Preparation of the complexes. All BF_4^- complexes were prepared by the method described by Van Leeuwen.[16] All $SbCl_6^-$ and $InCl_4^-$ complexes were prepared by the method described by Driessen.[13,14] Most of the complexes are hygroscopic and must be handled in a dried glove-box.

Measurements. Semi-micro metal analyses were carried out by complexometric titrations, as described by Vogel[17] and Schwarzenbach.[18] Element analyses (C, H and N) were carried out under supervision of Mr. W.J. Buis at the Micro-Analytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

X-ray powder diagrams of the compounds were obtained with a Guinier type powder camera using Cu-Kα radiation. The samples were mulled with vaseline and protected from atmospheric vapour by adhesive tape.

Infrared spectra in the 4000-400 cm^{-1} region were recorded on an Unicam SP.1200 spectrophotometer. The samples were measured as nujol mulls sandwiched between potassium bromide plates. Absorptions were calibrated against polystyrene.[19] Infrared spectra in the 700-200 cm^{-1} region were measured on a Hitachi EPI-L spectrophotometer as nujol mulls between polythene plates, using equal thickness of polythene in the reference beam of the apparatus. Water vapour served as a calibrant in this region.[20]

Diffuse reflectance spectra of the solid compounds were recorded on a Beckman DK-2A ratio recording spectrophotometer (2500-350 nm), equipped with a standard reflectance attachment. Samples of moisture-sensitive compounds were prepared in a dried glove-box, and protected against moist air in a sample holder as described by Van Leeuwen.[21] Spectra were measured by the double-beam technique, with magnesium oxide as a reference. Transmission spectra were recorded with the same apparatus, using a 1 cm silica cell, with the pure solvent as a reference.

Conductivity measurements were carried out with a Philips cell, type GM 4221, and a Philips conductivity bridge, type 4249.

Results and Discussion

Section I. The complexes. In Table I the ligands investigated in the present work are listed together with their abbreviations. In Table II the new complexes are tabulated with their colours, melting points and analytical data; details about the other complexes can be found in refs. 13, 14.

Table I. Carbonyl ligands (R_1R_2CO) investigated in the present work.

Description	R_1	R_2	Abbreviation
Acetaldehyde	H	CH_3	AA
Propionaldehyde	H	C_2H_5	PA
Benzaldehyde	H	C_6H_5	BA
Methylformate	H	OCH_3	MF
Formamide	H	NH_2	FA
N,N-dimethylformamide	H	$N(CH_3)_2$	DMF
Acetone	CH_3	CH_3	A
Chloroacetone	CH_3	CH_2Cl	CA
Butanone	CH_3	C_2H_5	BN
Acetophenone	CH_3	C_6H_5	AF
Ethylacetate	CH_3	OC_2H_5	EA
Acetamide	CH_3	NH_2	AAM
N,N-dimethylacetamide	CH_3	$N(CH_3)_2$	DMA
Acetanilide	CH_3	$N(H)C_6H_5$	AAN
Chloroacetamide	NH_2	CH_2Cl	CAM
Trimethylacetamide	NH_2	$C(CH_3)_3$	TMAM
Benzamide	NH_2	C_5H_5	BAM
Nictotineamide	NH_2	C_5H_4N	NAM
2-Nitrobenzamide	NH_2	$C_6H_4NO_2$	ONBA
2,6-Dichlorobenzamide	NH_2	$C_6H_3Cl_2$	DCBA
Urethane	NH_2	OC_2H_5	UT
Urea	NH_2	NH_2	U
Dimethylcarbamoylcloride	$N(CH_3)_3$	Cl	DMCC

With the ligands FA, DMCC, DCBA, and ONBA, no solid complexes could be prepared. In the case of DCBA and ONBA, the reason might be a steric effect.[22] In the case of FA and DMCC, complex formation does occur (*i.e.* a colour change of the metal salt solution took place upon addition of the ligand); we are here thus dealing with a crystallization problem. With NAM solid complexes could be prepared. However, coordination appeared to take place *via* the pyridine-N atom (*cf.* refs. 23, 24); consequently this ligand was not investigated any further.

Infrared spectra showed that in all complexes the C=O stretching vibration is shifted to lower frequencies compared with the frequencies of the C=O stretching vibrations in the free ligands. This indicates that coordination has occurred through the carbonyl oxygen atom of the ligands.[13,14,19]

The far infrared spectra of the $SbCl_6^-$ complexes all showed a strong and rather broad band at about 345 cm^{-1}. This band is characteristic for the $SbCl_6^-$ ion and has been assigned to the $\nu_3(t_{1u})$ mode of this octahedral.[13,14,19] The spectra of the tetrafluoroborato complexes showed the vibrations usually found for uncoordinated BF_4^- ions.[12,19]

Of further interest are the metal-ligand stretching vibrations, since the positions of these bands for the various complexes might give an indication about the relative ligand strength. Unfortunately we were un-

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Table II. New carbonyl complexes; their analyses, melting points and colours

Compound	% M^{II} Found	Calcd	Colour	Melting point (°C)
$Mn(U)_6(BF_4)_2$	9.37	9.33	white	178 dec.
$Co(U)_6(BF_4)_2$	9.94	9.94	red	168-170
$Ni(U)_6(BF_4)_2$	9.93	9.91	green	176 dec.
$Zn(U)_6(BF_4)_2$	11.2	10.9	white	138 dec.
$Cd(U)_6(BF_4)_2$	17.4	17.4	white	147-149
$Mn(UT)_6(SbCl_6)_2$	4.20	4.37	white	190 dec.[a]
$Co(UT)_6(SbCl_6)_2$	4.64	4.67	pink	199-201
$Ni(UT)_6(SbCl_6)_2$	4.64	4.65	light green	208 dec.
$Zn(UT)_6(SbCl_6)_2$	5.11	5.15	white	158-160
$Cd(UT)_6(SbCl_6)_2$	8.52	8.54	white	140 dec.[b]
$Mn(CAM)_6(SbCl_6)_2$	4.30	4.28	yellow	260 dec.[c]
$Co(CAM)_6(SbCl_6)_2$	4.59	4.57	pink	260 dec.
$Ni(CAM)_6(SbCl_6)_2$	4.54	4.56	light green	252 dec.
$Zn(CAM)_6(SbCl_6)_2$	5.03	5.05	white	215-217
$Cd(CAM)_6(SbCl_6)_2$	8.39	8.37	white	194-196
$Co(DMF)_6(BF_4)_2$	8.81	8.78	red	120-122
$Ni(DMF)_6(BF_4)_2$	8.82	8.75	green	142-144
$Zn(DMF)_6(BF_4)_2$	9.42	9.65	white	92-95
$Co(AAM)_6(BF_4)_2$	10.2	10.0	red	152-156
$Ni(AAM)_6(BF_4)_2$	10.4	10.0	light green	190-192
$Cd(AAM)_6(BF_4)_2$	17.9	17.6	white	95-98
$Co(DMA)_6(BF_4)_2$	8.00	7.80	purple-red	84-86
$Ni(DMA)_6(BF_4)_2$	7.90	7.76	yellow	105-110
$Cd(DMA)_6(BF_4)_2$	14.2	13.9	white	120-122
$Co(BAM)_6(BF_4)_2$	6.29	6.14	red	230-238
$Ni(BAM)_6(BF_4)_2$	6.33	6.12	light green	249-251
$Zn(BAM)_6(BF_4)_2$	6.58	6.77	white	201-203
$Co(AAN)_6(BF_4)_2$	5.81	5.65	red	249-251
$Ni(AAN)_6(BF_4)_2$	5.79	5.63	light green	249-251
$Co(TMAM)_6(BF_4)_2$	6.72	7.02	pink	248-251
$Ni(TMAM)_6(BF_4)_2$	6.89	7.00	light green	249-251

[a] %C: 16.4 (calcd 17.2), %H: (calcd 3.36), %N: 6.42 (calcd 6.68). [b] %C: 16.4 (calcd 16.4). %H: 3.19 (calcd 3.22), %N: 6.37 (calcd 6.39). [c] %C: 11.2 (calcd 11.2), %H: 1.94 (calcd 1.88), %N: 6.58 (calcd 6.54).

able to assign these bands definitely for all complexes (*cf.* refs. 13, 14).

As can be seen from Table II, all complexes contain six carbonyl molecules per divalent cation. Infrared spectroscopy showed that all ligand molecules in a complex are equivalent and coordinated *via* the carbonyl oxygen atom; furthermore these spectra indicated uncoordinated anions. The band positions in the ligand-field spectra of the Co^{II} and Ni^{II} complexes agreed with octahedral symmetry of the cations (see also section II). Furthermore, the X-ray powder patterns showed that al complexes of a given ligand were isomorphous.

It can therefore be concluded that all complexes listed in Table II are octahedral solvates and can be formulated as $[M(ligand)_6]^{2+}(Anion^-)_2$.

Finally, it is remarked that with the ligands U, DMF, AAN, DMA, BAM, AAM, and TMAM, hexakis metal(II) perchlorate complexes have been reported in the literature.[2,9,10,21,25-28]

Section II. Ligand-field and substituent parameters. For evidence about the coordination around the metal ions and the ligand-field strengths of the carbonyl compounds, ligand-field spectra of the Co^{II} (in the solid state) and the Ni^{II} complexes (both in the solid state and in nitromethane solution) were taken.

The band positions in the ligand-field spectra of the Co^{II} complexes are in agreement with octahedral symmetry of the cations. The methods of calculation for the parameters Dq and B from the ligand-field spectra of octahedral Co^{II} complexes were discussed by Reedijk *et al.*[29] These authors introduced a new method, which considers the lowering of the $^4T_{1g}(F)$ state by spin-orbit splitting. In Table III the band maxima, assignments and calculated parameters are listed. For details on the calculation method, we refer to the original paper by Reedijk *et al.*[29]

The ligand-field spectra of the Ni^{II} complexes also correspond with octahedrally surrounded metal ions, both for the solid and solution measurements. It seems appropriate to mention the way the solutions were made: Solutions of the BF_4^- complexes were prepared by dissolving the solid complexes in dry CH_3NO_2. Solutions of the $SbCl_6^-$ complexes were prepared by adding the ligand to a solution of $Ni(CH_3NO_2)_6(SbCl_6)_2$ in CH_3NO_2 (*cf.* refs. 13, 30). In some cases this resulted in decomposition of the complexes; nevertheless measurements were possible in most cases. Whenever possible, metal to ligand ratios of 1:6 and 1:8 were taken, besides a measurement with a large excess of ligand. Finally, it is remarked that all solutions were about 0.05 molar.

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Table III. Ligand-field spectra of solid cobalt(II) carbonyl co mplexes.

Compound	Band maxima (kK) and assignments* ν_1	ν_2	ν_3	Dq cm^{-1}	B cm^{-1}
$Co(AA)_6(InCl_4)_2$	8.68	16.4 sh	19.7	948	805
$Co(PA)_6(InCl_4)_2$	8.67	16.2	20.0	947	830
$Co(BA)_6(SbCl_6)_2$	8.74	16.1	20.2	954	840
$Co(MF)_6(InCl_4)_2$	8.10	16.2 sh	19.6	883	839
$Co(DMF)_6BF_4)_2$	8.17	—	19.4	891	823
$Co(A)_6(InCl_4)_2$	7.90	15.3 sh	19.0	862	811
$Co(CA)_6(InCl_4)_2$	7.73	15.3 sh	19.1	842	827
$Co(BN)_6(InCl_4)_2$	7.57	15.8 sh	18.9	824	824
$Co(AF)_6(InCl_4)_2$	7.47	15.8 sh	19.4	810	866
$Co(EA)_6(SbCl_6)_2$	7.30	14.4 sh	18.9	792	841
$Co(AAM)_6(BF_4)_2$	8.06	—	19.3	879	824
$Co(DMA)_6(BF_4)_2$	6.98	13.8	18.5	755	835
$Co(AAN)_6(BF_4)_2$	8.05	—	19.2	878	817
$Co(CAM)_6(SbCl_6)_2$	8.44	15.4	19.7	922	821
$Co(TMAM)_6(BF_4)_2$	8.30	—	19.3	906	806
$Co(BAM)_6(BF_4)_2$	8.08	14.9	19.3	881	821
$Co(UT)_6(SbCl_6)_2$	7.87	15.4	19.3	857	831
$Co(U)_6(BF_4)_2$	7.59	15.4	19.1	825	836

*: $\nu_1 = {}^4T_{2g} \leftarrow {}^4T_{1g}(F)$, $\nu_2 = {}^4A_{2g} \leftarrow {}^4T_{1g}(F)$, $\nu_3 = {}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$.

Table IV. Ligand-field spectra o nickel(II) carbonyl complexes.

Compound	State	Band maxima (kK) and assignments [a,b] * ν_1	ν_2	ν_4	ν_3	Dq [b] cm^{-1}	B [b,c] cm^{-1}
$Ni(AA)_6(InCl_4)_2$	Solid	9.44	16.0	13.9 sh	—	944	[891]
$Ni(AA)_6(SbCl_6)_2$	In CH_3NO_2	8.62 (8.70)	15.3	13.6	—	862 (870)	[862]
$Ni(PA)_6(InCl_4)_2$	Solid	9.39	15.8	13.6 sh	26.5	939	919
$Ni(PA)_6(SbCl_6)_2$	In CH_3NO_2	8.70 (8.58)	15.3	13.8	—	870 (858)	[853]
$Ni(BA)_6(SbCl_6)_2$	Solid	9.48	15.9	13.4 sh	—	948	[900]
$Ni(BA)_6(SbCl)_6)_2$	In CH_3NO_2	8.89 (8.93)	15.4	13.5	—	889 (893)	[855]
$Ni(MF)_6(InCl_4)_2$	Solid	8.80	15.2	13.9	25.5	880	911
$Ni(MF)_6(SbCl_6)_2$	In CH_3NO_2	8.40 (8.40)	14.3 (13.9)	14.3 (14.9)	—	840 (840)	[884][(894)]
$Ni(DMF)_6(BF_4)_2$	Solid	8.77	15.1	13.8	25.6	877	919
$Ni(DMF)_6(BF_4)_2$	In CH_3NO_2	8.53	14.9	13.6	—	853	[889]
$Ni(DMF)_6(SbCl_6)_2$	In CH_3NO_2	8.45 (8.30)	14.2 (14.8)	14.2 (13.6)	—	845 (830)	[889][(865)]
$Ni(A)_6(InCl_4)_2$	Solid	8.60	15.2	13.9	24.8	860	882
$Ni(A)_6(SbCl_6)_2$	In CH_3NO_2	8.16 (8.16)	13.5	14.9	—	816 (816)	[877]
$Ni(CA)_6(InCl_4)_2$	Solid	8.39	13.4	14.6	24.8	839	901
$Ni(CA)_6(SbCl_6)_2$	In CH_3NO_2	8.10 (8.10)	14.6	13.3	—	810 (810)	[844]
$Ni(BN)_6(InCl_4)_2$	Solid	8.20	13.9	14.8	24.5	820	905
$Ni(BN)_6(SbCl_6)_2$	In CH_3NO_2	8.06 (8.03)	13.4	14.5	—	806 (803)	[867]
$Ni(AF)_6(InCl_4)_2$	Solid	8.10	15.4	13.8	—	810	[844]
$Ni(AF)_6(SbCl_6)_2$	In CH_3NO_2	8.00 (8.00)	13.4 (13.3)	14.5 (14.5)	—	800 (800)	[860][(860)]
$Ni(EA)_6(SbCl_6)_2$	Solid	7.95	13.2	14.8 sh	—	795	[903]
$Ni(EA)_6(SbCl_6)_2$	In CH_3NO_2	8.03 (8.05)	13.2 (13.3)	14.8 (14.6)	—	803 (805)	[934][(915)]
$Ni(AAM)_6(BF_4)_2$	Solid	8.64	13.7	15.0	23.6	864	920
$Ni(AAM)_6(BF_4)_2$	In CH_3NO_2	8.33	13.5	14.7	—	833	[896]
$Ni(AAM)_6(SbCl_4)_2$	In CH_3NO_2	8.21 (8.22)	13.4 (13.3)	14.6 (14.4)	—	821 (822)	[883][(884)]
$Ni(DMA)_6(BF_4)_2$	Solid	7.29	12.4	14.5	23.4	729	923
$Ni(AAN)_6(BF_4)_2$	Solid	8.33	13.3	14.7	24.7	833	903
$Ni(AAN)_6(BF_4)_2$	In CH_3NO_2	8.23	13.7	15.1	—	823	[895]
$Ni(CAM)_6(SbCl_6)_2$	Solid	8.44	15.1	13.6	—	844	[870]
$Ni(TMAM)_6(BF_4)_2$	Solid	8.50	13.9	13.9	24.9	850	902
$Ni(BAM)_6(BF_4)_2$	Solid	8.61	14.6	13.4	25.2	861	909
$Ni(BAM_6(SbCl_6)_2$	In CH_3NO_2	8.31 (8.33)	13.5 (13.6)	15.1 (14.4)	—	831 (833)	[894][(894)]
$Ni(UT_6(SbCl_6)_2$	Solid	8.24	13.4	14.8	—	824	[916]
$Ni(U)_6(BF_4)_2$	Solid	8.10	13.1	14.5 sh	24.7	810	929

[a] $\nu_1 = {}^3T_{2g} \leftarrow {}^3A_{2g}$, $\nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g}$, $\nu_3 = {}^3T_{1g}(P) \leftarrow {}^3A_{2g}$, $\nu_4 = {}^1E_g \leftarrow {}^3A_{2g}$. [b] Values in parentheses are for solutions with excess ligand (M:L = 1:8); solutions are about 0.05 molar. [c] Values in brackets were estimated from the band-shape (see ref. 31).

Reedijk *et al.*[31] elaborately discussed the calculation of the ligand-field parameters from the spectra of octahedrally coordinated Ni^{2+} ions. For details on the calculation method, we refer to this paper. It is however remarked that in the case of the $SbCl_6^-$ and some of the $InCl_4^-$ complexes, the "third" band (ν_3) is hidden under charge-transfer absorptions. In these cases the parameter B had to be calculated from the "band-shape".[31] In Table IV, the band maxima, assignments and calculated parameters are listed.

As regards the accurracies of the calculated ligand-field parameters, the following remarks can be made:

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(31) J. Reedijk, P.W.N.M. van Leeuwen and W.L. Groeneveld, *Rec. Trav. Chim.*, *87*, 129 (1968).

It was noted by Ferguson[32] that reliable absolute values for the parameters cannot possibly be obtained due to all kinds of perturbations on the original (simple) model (*e.g.* low-symmetry fields). However, if one calculates a number of these parameters, relative to the same metal ion, from spectra of the same type of compounds, and all measured in the same way, it will be possible to compare these parameters. So, if the parameters are solely used for comparison purposes, we believe that the accurracies, determined by the measurement limitations and similar errors, will be about 2% for Dq, 2% for B, and 4% for B determined from the "band-shape". (For the sake of completeness, it is remarked that spectra of the uncoloured compounds were taken to get an indication about the presence of infrared overtones in the regions of interest).

For a discussion of the influence of electronic properties of substituents on the donor properties of ligands, it is of course necessary to define parameters describing certain electronic effects of the substituents. The parameters which are the most appropriate for this purpose, are the Hammett σ constants. However, more than 20 σ sets are now in use, most of them being based experimentally on a single reaction series.[33] Swain and Lupton[33] elaborately discussed the various sets, and calculated two new constants, *F* (the field constant) and *R* (the resonance constant), which are, according to them, "more accurately defined and more physically signicant independent variables for correlating or predicting substituent effects on all kinds of physical properties than any other pair considered". They showed that all earlier constants could be linearly expressed in the new constants: $\sigma = \mathrm{f}F + \mathrm{r}R + \mathrm{p}$.

It seemed therefore most appropriate to attempt a linear correlation of the type $\mathrm{Dq(B)}_{\mathrm{R_1R_2CO}} = \mathrm{a}(F_{\mathrm{R_1}} + F_{\mathrm{R_2}}) + \mathrm{b}(R_{\mathrm{R_1}} + R_{\mathrm{R_2}}) + \mathrm{c}$, since in that case every correlation of the type $\mathrm{Dq(B)} = \mathrm{k}\sigma + 1$, leads to the same expression.

The values for the *F* and *R* substituent constants that we used are presented in Table V (they are due to Swain and Lupton[33]). As can be seen from this table, no data are available for the substituents CH_2-Cl and $N(CH_3)_2$. It appeared to be possible to calculate (from data in ref. 33) *F* and *R* values for these substituents ($F_{\mathrm{CH_2Cl}} = 0.250$, $R_{\mathrm{CH_2Cl}} = -0.020$, $F_{\mathrm{N(CH_3)_2}} = -0.109$, $R_{\mathrm{N(CH_3)_2}} = -0.541$), but we decided not to use them in the correlations but only as a means of "checking".

A computerized general-purpose linear least-squares multiple correlation analysis was used to determine the best values of *a, b,* and *c,* standard deviations, and correlation coefficients. Several sets (solid, 1:6 and 1:8 solutions) and selections of Dq and B values were used in the correlations.

However, with selection of 9 (Dq or B) values or more, no significant correlation (*i.e.* with correlation coefficients (=C) of 0.900 or greater) was found (with one exception, to be discussed below). When small selections (5 values or less) of Dq and B values (so selected that R_1 = constant) were used, correlation coefficients of 0.900 or greater were obtained in some cases, but since these correlations are based on such small selections they can hardly be called physically significant. Some typical results for Ni^{II} are presented in Table VI.

Table V. Field (*F*) and resonance (*R*) substituent constants.*

Substituent	*F*	*R*
H	0.000	0.000
CH_3	–0.052	–0.141
C_2H_5	–0.065	–0.114
C_6H_5	0.139	–0.088
OCH_3	0.413	–0.500
OC_2H_5	0.363	–0.444
$C(CH_3)_3$	–0.104	–0.138
NH_2	0.037	–0.681

* Duc to Swain and Lupton.[33]

As can be seen from this table, one "complete" selection (B of Ni^{2+} for 1:6 solution) did give a significant correlation coefficient, but as this appeared to be the only one of the group, the results cannot be interpreted as indicating a positive correlation.

It can therefore be concluded that ligand-field parameters for Ni^{II} and Co^{II} carbonyl complexes in both the solid state and in nitromethane solution do not correlate linearly with electronic parameters of the subsituents.

For the sake of completeness, it is remarked that the same holds for Dq/B, and that the relation $\mathrm{k}\sigma + 1$ was also checked graphically (with the same, negative, result).

It follows then that the variation of the ligand-field parameters with the carbonyl ligands is caused by (at least for a significant part) steric effects. It is thus seen that the same conclusion as reached by Drago[2,6] for amide complexes, holds for this large group of ligands.

As regards the relative values for the ligand-field parameters, the following remarks can be made:

1. There is no significant difference between the parameters for the 1:6 and 1:8 solutions (the solutions with a large excess of ligand also gave the same results). This indicates that the group $Ni(Ligand)_6^{2+}$ is also present in the solutions. This is supported by results from conductivity measurements: The molar conductivities for the 1:6 solutions of $Ni(EA)_6(SbCl_6)_2$, $Ni(AAM)_6(SbCl_6)_2$, $Ni(MF)_6(SbCl_6)_2$ and $Ni(BAM)_6(SbCl_6)_2$ were found to be 316, 376, 262 and 286 $cm^2\ \Omega^{-1}\ mol^{-1}$, respectively; these values are all in the range expected for 1:2 electrolytes.[34,35] It is further remarked that a variation of anion did not significantly influence the ligand-field spectra (compare *e.g.* $Ni(AAM)_6(BF_4)_2$ and $Ni(AAM)_6(SbCl_6)_2$); this supports the conclusions above.

2. The Dq values for the solid Ni^{2+} complexes are almost invariably larger than those for the corresponding complexes in nitromethane solution. This can

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[32] J. Ferguson, Spectroscopy of 3*d* Complexes, Progress in Inorganic Chemistry, Edited by S.J. Lippard, Volume 12, p. 159, Interscience, New York, 1970.

[33] C.G. Swain and E.C. Lupton Jr., *J. Am. Chem. Soc., 90,* 4328 (1968).

[34] W. Libus and D. Puchaska, *J. Phys. Chem., 71,* 3549 (1967).

[35] J.H. Nelson, L.C. Nathan, and R.O. Ragsdale, *Inorg. Chem.,* 7, 1840 (1968).

Table VI. Correlation of Dq, B *vs.* *F* and *R* for complexes of the type $Ni(R_1R_2CO)_6(Anion)_2$.

Ligand	R_1	R_2	Dq_F [k]	Dq_C [a]	B_F [l]	B_C [b]	Dq_F [m]	Dq_C [c]	B_F [n]	B_C [d]
PA	H	CH_3	944	892	862	860	n.u.	—	891	905
AA	H	C_2H_5	939	895	853	858	n.u.	—	919	905
BA	H	C_6H_5	948	894	855	857	n.u.	—	900	901
MF	H	OCH_3	880	861	884	880	n.u.	—	911	910
A	CH_3	CH_3	860	883	877	868	n.u.	—	n.u.	—
BN	CH_3	C_2H_5	820	885	867	866	n.u.	—	n.u.	—
AF	CH_3	C_6H_5	810	884	860	865	n.u.	—	n.u.	—
EA	CH_3	OC_2H_5	795	856	n.u.	—	n.u.	—	n.u.	—
AAM	CH_3	NH_2	864	844	896	894	864	857	n.u.	—
TMAM	NH_2	$C(CH_3)_3$	850	845	n.u.	—	850	858	n.u.	—
BAM	NH_2	C_6H_5	861	845	894	895	861	859	n.u.	—
UT	NH_2	OC_2H_5	824	817	n.u.	—	824	826	n.u.	—
U	NH_2	NH_2	810	804	n.u.	—	810	809	n.u.	—

f = Found; c = calculated; n.u. = not used in the correlation. [k] Dq solid; [l] B of 1.6 solution; [m] Dq solid; [n] *B* solid. [a] Calculated from the equation $Dq = -13.5(F_{R_1}+F_{R_2}) + 70.8(R_{R_1}+R_{R_2}) + 901$ (C = 0.567). [b] Calculated from the equation $B = -$ $-0.558\ (F_{R_1}+F_{R_2}) - 56.8\ (R_{R_1}+R_{R_2}) + 852$ (C= 0.960). [c] Calculated from the equation $Dq = -11.0\ (F_{R_1}+F_{R_2}) + 87.4$ $R_{R_1}+R_{R_2}) + 929$ (C = 0.973). [d] Calculated from the equation $B -12.4\ (F_{R_1}+F_{R_2}) - 29.7\ (R_{R_1}+R_{R_2}) + 900$ (C = 0.300).

be interpreted as indicating that the lattice exerts a certain "pressure" on the group $Ni(ligand)_6^{2+}$. With some exceptions (which may be due to the measurement error) the same holds for B.

3. According to Drago,[2,6] the variation in Dq (for amide complexes) is caused by interaction of neighbouring ligand groups, *i.e.* R_1 *vs.* R_2 (for R_1R_2CO complexes). Our Dq values seem to be in accordance with this proposition. The aldehydes, for instance, show high Dq values. However, the Dq values for AAM (R_1 = CH_3, R_2 = NH_2) and TMAM (R_1 = $C(CH_3)_3$, R_2 = NH_2) are hardly different. This agrees with earlier results of Cunningham *et al.*,[10] who explained this observation by saying "that there is apparently sufficient space in the coordination sphere to allow for the increased bulk without affecting the amides ability to coordinate". If one considers Table IV more closely, one can find more of such discrepancies (*e.g.* MF *vs.* BA). This can be interpreted as indicating that electronic effects still play a role in determining Dq and B. In this connection it is interesting to note that our correlations attempts (of the type $Dq(B) = a(F_{R_1}+F_{R_2})+b(R_{R_1}+R_{R_2})+c$) showed the parameter *b* to be almost invariably larger than *a*. It can therefore be concluded that if electronic effects play a role, the resonance effect is relatively more important than the field effect.

If we compare the results found here with those obtained for phosphine oxides,[11,12] it can be said that carbonyl complexes (with a considerable variation in the ligand-field parameters) show a widely different behaviour than phosphoryl complexes (with almost no variation in the ligand-field parameters). We are inclined to explain this by the difference in steric build of the ligand skeletons ("planar" *vs.* "tetrahedral") which will induce steric effects to be more important in the carbonyl case. Finally, it is noted that the fact that carbonyl ligands are more nephelauxetic than phosphoryl ligands might cause electronic effects to be more important in the carbonyl case.

Conclusions

From the results discussed above, the following conclusions can be drawn:

1. Carbonyl compounds are rather strongly coordinating ligands towards bivalent transition metal ions, yielding octahedrally solvated MO_6^{2+} species.

2. No linear correlation exists between the ligand-field parameters (relative to cobalt(II) and nickel(II)) and parameters describing certain electronic effects of substituents.

3. The significant variations in the ligand-field parameters for the various complexes are mainly caused by steric effects.

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