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Synthesis, Structure and Properties of the Chromium Nitrosyl Complexes of $[CrNO(CN)_x(en)_y]^{n\pm}$ Type

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The series of the nitrosyl chromium complexes of types $[CrNO(CN)_x(en)_y]^{n\pm}$ were synthesized and investigated: I, $K[CrNO(CN)_2(en)(OH)]\cdot 4H_2O$; II, $[CrNO(CN)_2(en)(H_2O)]$; III, $Cr_2(NO)_2(CN)_4(en)_3]$; IV, $[Cr_2(NO)_2(CN)_2(en)_4]Cl_2\cdot 2H_2O$; V, $[Cr_2(NO)_2(en)_5]Cl_4\cdot 6H_2O$. The complexes III–V were found to be the dimers which bridge ethylenediamine Their structure was determined by the magnetic and spectroscopic (EPR, UV-VIS and IR) methods. The influence of the coordinated ligands upon the electronic structure of the molecular unit {CrNO} was determined.

Introduction

The acid hydrolysis of the chromium pentacyanonitrosyl complex leads to the formation of compounds of a general formula $[CrNO(CN)_{6-x}L_x]$ ($L = H_2O$) [1–3].

New compounds of this type where L = ethylenediamine (en) have been synthesized. Those complexes are convenient for the study of the influence of ligands on the electron structure of the molecular unit {Cr-NO}. The investigations were based upon measurements of magnetic properties and upon the analysis of vibrational and absorption electronic spectra as well as the EPR method.

Experimental

Synthesis of $K[CrNO(CN)_2(en)(OH)]\cdot H_2O$ (I)

45 ml ethylenediamine was added dosewise to a solution of 7 g CrO_3 in 20 ml H_2O cooled to 0 °C. A solution of KCN (16 g in 30 ml H_2O) was added. This solution was then heated and a solution of 9 g of hydroxylamine in a minimum amount of water was added. The brown-yellow solution of the complex was cooled and treated with n-propyl alcohol. The oily complex isolated was solidified on the addition of absolute ethyl alcohol. The crude product was repeatedly recrystallized. The pure complex was dried over P_2O_5. *Analysis* for $K[CrNO(CN)_2(en)(OH)]\cdot H_2O$: Calcd. K, 14.57; Cr, 19.39; CN, 19.40; C, 17.91; N, 26.11%. Found: K, 14.62; Cr, 19.30; CN, 19.29; C, 17.99; N, 25.91%.

Synthesis of $[CrNO(CN)_2(en)(H_2O)]$ (II)

$[CrNO(CN)_2(en)(H_2O)]$ was obtained in the reaction:

$$[CrNO(CN)_2(en)(OH)]^- + H_2O \rightleftharpoons [CrNO(CN)_2(en)(H_2O)] + OH^-$$

The hydrogen ions cause a shift of the equilibrium to the right-hand side, but at pH < 7 a decomposition of the initial complex occurs. The pink precipitate was dried over P_2O_5. *Analysis* for $[CrNO(CN)_2(en)(H_2O)]$: Calcd. Cr, 24.51; CN^-, 24.53; C, 22.64; N, 33.01; H, 4.75%. Found Cr, 24.60; CN^-, 24.45; C, 22.72; N, 32.90; H, 4.68%.

Synthesis of $[Cr_2(NO)_2(CN)_4(en)_3]$ (III)

The complex $[Cr_2(NO)_2(en)_5]Cl_4$ (V) was dissolved in methanol. A solution of NaCN in CH_3OH was added ($Cr:CN^- = 1:2$), and the mixture was left for 24 h. The isolated brown precipitate was mixed with methanol and placed under vacuum. *Analysis* for $[Cr_2(NO)_2(CN)_4(en)_3]$: Calcd. Cr, 23.25; CN^-, 23.21; N, 37.49; C, 26.78; H, 5.39%. Found Cr, 23.28; CN^-, 23.14; N, 37.2; C, 26.70; H, 5.44%.

Synthesis of $[Cr_2(NO)_2(CN)_2(en)_4]Cl_2\cdot 2H_2O$ (IV)

The compound was synthesized as the complex (I). The only difference was that only 4.6 g KCN in 15 ml H_2O was added. The crude product was isolated by the addition of absolute ethyl alcohol. After repeated recrystallization the light brown precipitate was washed with methanol and dried under vacuum over P_2O_5. *Analysis* for $[Cr_2(NO)_2(CN)_2(en)_4]Cl_2\cdot 2H_2O$: Calcd. Cr, 17.35; CN, 8.68; N, 28.04; C, 20.04; H, 6.73; Cl^-, 11.83%. Found Cr, 17.39; CN, 8.59; N, 27.90; C, 20.11; H, 6.82; Cl^-, 11.94%.

Synthesis of $[Cr_2(NO)_2(en)_5]Cl_4 \cdot 6H_2O$ *(V)*

35 ml ethylenediamine and 9 g of an aqueous solution of hydroxylamine hydrochloride were added slowly to a cooled (about 0 ℃) solution of 7 g CrO_3 in 10 ml H_2O. The reaction mixture was heated on a water bath for 1 h. Propyl alcohol was then added to the cooled red solution of the complex. The oily substance formed was washed with n-propyl alcohol and dissolved in CH_3OH. The methanol solution was neutralized with HCl in CH_3OH. The complex was precipitated with absolute ethyl alcohol, washed and dried over P_2O_5. *Analysis* for $[Cr_2(NO)_2(en)_5]Cl_4 \cdot 6H_2O$: Calcd. Cr, 12.65; Cl^-, 17.24; N, 20.44; C, 14.60; H, 7.84%. Found Cr, 12.60; Cl^-, 17.32; N, 20.38; C, 14.69; H, 7.98%.

Synthesis of $[Cr_2(NO)_2(CN)_2(en)_4][B(Ph)_4]_2$ *(IVa) and* $[Cr_2(NO)_2(en)_5]\,[B(Ph)_4]_4$ *(Va)*

The tetraphenylborane salts of complexes (IV) and (V) were synthetized by precipitation of the appropriate ions from aqueous solutions by sodium tetraphenylborane. *Analysis* for $[Cr_2(NO)_2(CN)_2(en)_4]\,[B(Ph)_4]_2$: Calcd. Cr, 9.50; C, 63.62; N, 15.35; H, 6.63%. Found Cr, 5.41; C, 63.83; N, 15.26; H, 6.70%. For $[Cr_2(NO)_2(en)_5]\,[B(Ph_4)]_4$: Calcd. Cr, 5.97; C, 73.11; N, 9.05; H, 6.95%. Found, Cr, 5.90; C, 75.25; N, 9.57; H, 6.89%.

Synthesis of the N-deuterated derivative of the complex $[Cr_2(NO)_2(en)_5]Cl_4$ *(Vb)*

The complex $[Cr_2(NO)_2(en)_5]Cl_4 \cdot 6H_2O$ (V) was dissolved in D_2O, and next evaporated under reduced pressure at 40 ℃. The procedure was repeated 5 times until the ν(OH) and ν(NH) bands in the IR spectra disappeared.

Synthesis of the Nonaqueous Complexes: $K[CrNO(CN)_2(en)(OH)]$, $[Cr_2(NO)_2(CN)_2(en)_4]Cl_2$, $[Cr(NO)_2(en)_5]Cl_4$ *and* $[Cr_2(NO)_2(enD)_5]Cl_4$

The anhydrous salts of complexes (I) (IV), (V), and (Vb) were obtained by drying under a reduced pressure at 70 ℃.

Synthesis of $K_3[CrNO(CN)_5] \cdot 3H_2O$ *(VI)*

$K_3[CrNO(CN)_5] \cdot 3H_2O$ was prepared by Griffith's method [4].

Instrumentation

Magnetic susceptibility measurements were made by the Gouy method over the temperature range 77–295 K. The EPR spectra were recorded on a JES-ME-3X X-band spectrometer at 125–320 K using Mn^{+2} in HgO and Fermi's salt as ESR standards and the JES-SH-3CX superheterodyne for microwave frequency measure. IR spectra were recorded over the range 200–4000 cm^{-1} with Perkin-Elmer spectrophotometers type 121 and 621 in KBr mulls and in Nujol.

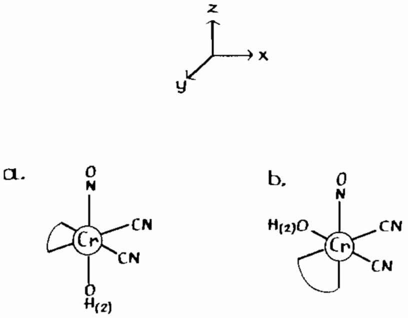

Fig. 1. The possible structures for the complexes (I) and (II).

The electronic absorption spectra were measured over the range 50000–10000 cm^{-1} with the Cary-14 spectrophotometer.

Results and Discussion

A series of chromium nitrosyl complexes, which are derivatives of the pentacyanonitrosyl complex with cyanate ligands replaced by ethylenediamine, were investigated. Five new complexes were synthesized and identified as:

I $K[CrNO(CN)_2(en)(OH)] \cdot H_2O$
(μ_{ef} = 1.96 MB, Θ = –14 K)
II $[CrNO(CN)_2(en)(H_2O)]$
(μ_{ef} = 1.94 MB, Θ = –20 K)
III $[Cr(NO)_2(CN)_4(en)_3]$
(μ_{ef} = 1.86 MB, Θ = –26 K)
IV $[Cr(NO_2(CN)_2(en)_4]Cl_2 \cdot 2H_2O$
(μ_{ef} = 1.90 MB, Θ = –30 K)
V $[Cr_2(NO)_2(en)_5]Cl_4 \cdot 6H_2O$
(μ_{ef} = 2.10 MB, Θ = –26 K)

The dimeric structure with bridging ethylenediamine was assigned to the complexes III–V on the basis of the elementary analysis and results of investigations given below. The μ_{ef} values were calculated for one atom of the metal.

Infrared Spectra

The complexes (I–V) were synthesized in the form of non-crystalline precipitates. Complexes I and II may have one of the two possible structures (Fig. 1 a, b), in which the OH or H_2O substituents are either in the *cis* or *trans* position in relation to the NO group. In both cases, however, the number of infrared active vibrations is identical. The distribution of these vibrations on the group vibration is shown in Table I. In Fig. 2 the most probable structures for the complexes III–V are shown. The Cr(en)-Cr arrangement, in which ethylenediamine is *trans* coordinated (C_{2h} symmetry), is the common element

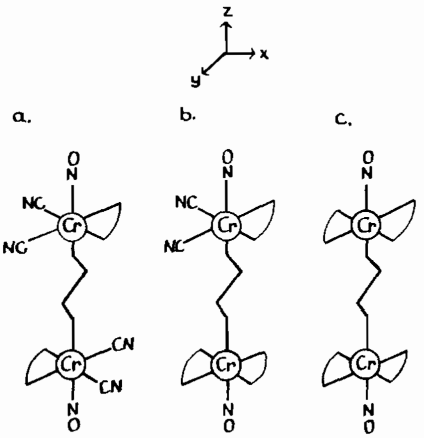

Fig. 2. The most probable structures for the complexes III–V.

of their structure. The kind and symmetry of vibrations for molecules of the complexes III and V are given in Table II. As, in the case of compounds I and II (Table I), the skeletals are not specified further because of the coupling between them.

From inspection of the data given in Tables I and II one learns that the number of infrared active vibrations of the Cr(en) group with the chelate coordinated ethylenediamine is equal in the complexes I, II and III as well as in III and V if an appropriate symmetry is assumed. A similar situation was observed for compounds of the type $[M(en)X_2]$ and $[Me(en)_2]X_2$ [5, 6].

The richest IR spectrum should be that of the complex IV which representation of 168 internal vibrations, assuming the C_s symmetry (Fig. 2b), decomposes as follows: $89A' + 79A''$. These vibrations are active both in the infrared and Raman spectra. Obviously, not all these vibrations are detectable.

In Table IV the frequencies observed in the IR spectra of the nonaqueous complexes I–V and Vb,

TABLE I. Distribution of Internal Group Vibrations of $[CrNO(CN)_2(en)(OH)]^-$ and $[CrNO(CN)_2(en)(H_2O)]$ (II) on Symmetry Types.

Point Group	C_s		C_1
Symmetry	A′	A″	A
Activity	IR + Ra.	IR + Ra.	IR + Ra.
OH str.	1	(1)[a]	1(2)[a]
NH str.	2	2	4
CH str.	2	2	4
NO str.	1	–	1
CN str.	1	1	2
CN(en) str.	1	1	2
CC str.	1	–	1
CrN(NO) str.	1	–	1
CrN(en) str.	1	1	2
CrC str.	1	1	2
CrO str.	1	–	1
NH_2 sci.	1	1	2
CH_2 sci.	1	1	2
H_2O sci.	1[a]	–	1[a]
CrNO sci.	1	–	1
$Cr(N)_2(en)$ sci	1	–	1
CrCN sci.	2	2	4
CrOH sci.	1[b]	–	1[b]
NH_2 twi.	1	1	2
CH_2 twi.	1	1	2
NH_2 wag.	1	1	2
CH_2 wag.	1	1	2
NH_2 rock.	1	1	2
CH_2 rock.	1	1	2
H_2O rock.	1[a]	1[a]	2[a]
ring def.	1	2	3
other def.	4	6	10
Total:			
for complex I	31	26	57
for complex II	32	28	60

[a] Only for complex II. [b] Only for complex I. The correlation from C_s to C_1 is: (A′ + A″) → (A).

TABLE II. Distribution of Internal Group Vibrations of $[Cr_2(NO)_2(CN)_4(en)_3]$ and $[Cr_2(NO)_2(en)_5]^{4-}$ on Symmetry Types.*

$[Cr_2(NO)_2(CN)_4(en)_3]$							$[Cr_2(NO)_2(en)_5]^{4-}$											
Point Group	C_2		C_{2h}				C_{2h}				D_{2h}							
Symmetry	A	B	Ag	Bg	Au	Bu	Ag	Bg	Au	Bu	Ag	B_{1g}	B_{2g}	B_{3g}	Au	B_{1u}	B_{2u}	B_{3u}
Activity	IR Ra.	IR Ra.	Ra.	Ra.	IR	IR	Ra.	Ra.	IR	IR	Ra.	Ra.	Ra.	Ra.	n.a.	IR	IR	IR
Cr–en–Cr	19	17	11	7	8	10	11	7	8	10	6	4	3	5	3	6	4	5
NH str.	4	4	2	2	2	2	4	4	4	4	2	2	2	2	2	2	2	2
CH str.	4	4	2	2	2	2	4	4	4	4	2	2	2	2	2	2	2	2
CN str.	2	2	1	1	1	1	–	–	–	–	–	–	–	–	–	–	–	–
CN(en) str.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
NO str.	1	1	1	–	–	1	1	–	–	1	1	–	–	–	–	1	–	–

(continued overleaf)

TABLE II. *(continued)*

$[Cr_2(NO)_2(CN)_4(en)_3]$							$[Cr_2(NO)_2(en)_5]^{4-}$											
Point Group	C_2		C_{2h}				C_{2h}				D_{2h}							
Symmetry Activity	A IR Ra.	B IR Ra.	Ag Ra.	Bg Ra.	Au IR	Bu IR	Ag Ra.	Bg Ra.	Au IR	Bu IR	Ag Ra.	B_{1g} Ra.	B_{2g} Ra.	B_{3g} Ra.	Au n.a.	B_{1u} IR	B_{2u} IR	B_{3u} IR
CC str.	1	1	1	–	–	1	2	–	–	2	1	–	–	1	–	1	1	–
CrN(NO) str.	1	1	1	–	–	1	1	–	–	1	1	–	–	–	–	1	–	–
CrN(en) str.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
CrC str.	2	2	1	1	1	1	–	–	–	–	–	–	–	–	–	–	–	–
NH_2 sci.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
CH_2 sci.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
CrNO sci.	1	1	1	–	–	1	1	–	–	1	1	–	–	–	–	1	–	–
CrCN sci.	4	4	2	2	2	2	–	–	–	–	–	–	–	–	–	–	–	–
NH_2 twi.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
CH_2 twi.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
NH_2wag.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
CH_2 wag.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
NH_2 rock.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
CH_2 rock.	2	2	1	1	1	1	2	2	2	2	1	1	1	1	1	1	1	1
ring. def. and other def.	14	14	5	9	9	5	7	10	10	7	2	2	8	5	4	1	6	6
Total	70	71	38	33	34	36	51	45	46	50	26	20	25	25	21	25	25	25

*Note that the correlation from C_{2h} to C_2 is: (Ag + Au) → A, (Bg + Bu) → B, and D_{2h} to C_{2h} is: (Ag + B_{3g}) → Ag, (B_{1g} + B_{2g}) → Bg, (Au + B_{3u}) → Au, (B_{1u} + B_{2u}) → Bu.

Ra. = Raman and IR = infrared.

TABLE III. Distribution of Internal Group Vibrations of $Cr-NH_2CH_2CH_2NH_2-Cr$ on Symmetry Types.

Point Group	C_{2h}				C_2	
Symmetry Activity	Ag Ra.	Bg Ra.	Au IR	Bu IR	A (Ra. + IR)	B
NH str.	1	1	1	1	2	2
CH str.	1	1	1	1	2	2
CN str.	1	–	–	1	1	1
CC str.	1	–	–	–	1	–
CrN str.	1	–	–	1	1	1
NH_2 sci.	1	–	–	1	1	1
CH_2 sci.	1	–	–	1	1	1
NCC sci.	1	–	–	1	1	1
CrNC sci.	1	–	–	1	1	1
NH_2 twi.	–	1	1	–	1	1
CH_2 twi.	–	1	1	–	1	1
NH_2 wag.	1	–	–	1	1	1
CH_2 wag.	1	–	–	1	1	1
NH_2 rock.	–	1	1	–	1	1
CH_2 rock.	–	1	1	–	1	1
π (NCCN)	–	–	1	–	1	1
π (CrNCC)	–	1	1	–	1	1
Total	11	7	8	10	19	17

attributed to the appropriate vibrations, are listed. The [M=(en)] group vibrations were identified on the basis of literature data concerning the IR spectra of transition metal complexes with ethylenediamine [5–12] and the ν(NH)/ν(ND) isotopic shifts in complexes V and Vb. The determined ν(NH)/ν(ND) ratio values are in agreement with those calculated theoretically [9].

The additional vibration frequencies of ethylenediamine in the IR spectra of the dimeric III, IV and V complexes which are not observed in spectra of the I and II monomers, may be assigned mainly to the ($Cr-NH_2CH_2CH_2NH_2-Cr$) group vibrations and in the case of the complex IV also to the increased amount of vibrations active in the infrared due to the chelate coordinated ethylenediamine. The regions of the appropriate group vibration frequencies of the chelate and bridge coordinated ethylenediamine are very close to each other. However, the analysis of the IR spectra of monomeric (I, II) and dimeric (III–V) complexes allows to distinguish some bands which should be obviously attributed to the vibrations of the bridging ethylenediamine. The corresponding frequencies are 950, 580, 510 and 410 cm^{-1}, assigned to the ν(CC), ν(CrN) vibrations and to the deformations of the (Cr–NCCN–Cr) core, respec-

TABLE IV. Assignments, Wavenumbers (cm^{-1}) and Frequency Ratios, (ν(NH)/ν(ND), of IR – active Transitions in Chromium Nitrosyl Compounds.

	I	II	III	IV	V	Vb	ν(NH)/ν(ND)
ν(OH)	3390 sh	3430 sh	–	–	–	–	–
		3395 s					
ν(NH)	3260 vs	3250 vs	3270 sh	3220 vs	3240 sh	2440 sh	1.33
	3130 sh	3130 vs	3220 vs		3200 vs	2405 vs	1.33
			3190 sh	3125 vs	3130 sh	2390 sh	1.31
			3130 vs		3110 vs	2300 vs	1.35
ν(CH)	2960 m	2950 m	2950 m	2960 s	2955 m	2955 m	
	2940 sh	2890 sh	2920 sh		2930 sh	2930 sh	
	2890 m	2845 sh	2880 w	2895 s	2890 m	2880 m	
	2850 sh		2850 sh		2870 sh	2850 sh	
					2850 sh		
$\delta(NH_2)$	1580 s	1575 s	1580 s	1595 sh	1595 sh	1285 sh	1.26
	1555 sh	1550 sh		1583 vs	1575 vs	1268 m	1.24
				1570 sh	1555 sh	1255 sh	1.24
				1555 sh			
$\delta(CH_2)$	1465 sh	1465 sh	1465 sh	1470 sh	1465 sh	1470 sh	
			1456 m	1455 s	1456 s	1455 s	
	1450 m	1451 m	1445 sh	1430 sh	1445 sh	1430 sh	
$\omega(CH_2)$	1390 sh	1389 w	1390 w	1393 w	1393 w	1375 w	
	1360 m	1360 w	1365 w	1370 sh	1365 w	1345 sh	
			1345 w	1363 w	1355 sh	1320 w	
				1345 w			
$\tau(CH_2)$	1330 sh	1330 m	1330 sh	1322 m	1325 m	1310 w	
			1320 m	1315 sh	1315 sh	1280 m	
	1280 m	1281 m	1282 m	1284 m	1287 m	1267 m	
$\omega(NH_2)$	1185 sh	1165 sh	1225 sh	1235 sh	1230 sh	935 sh	1.31
			1180 m	1185 m	1185 m	921 s	1.29
	1167 m		1170 sh	1165 sh	1170 sh	910 sh	1.29
$\tau(NH_2)$	1125 sh	1125 sh	1135 sh	1135 sh	1140 sh	830 sh	1.37
			1115 s	1120 s	1125 s	810 m	1.35
	1112 s	1110 s	1095 sh	1100 sh	1100 sh	795 sh	1.38
ν(CN)(en)	1044 vs	1044 vs	1045 vs	1048 vs	1049 vs	1047 vs	
				1015 sh			
	1008 m	1005 m	1008 m	1008 m	1008 m	1012 m	
ν(CC)	975 m	978 m	970 m	985 m	990 m	970 sh	
			940 sh	950 sh	955 vw		
$\rho(CH_2)$	877 w	874 w	880 vw	880 w	878 w	882 w	
	860 vw	855 w	865 vw	870 sh	863 sh	865 sh	
			830 vw	830 vw	830 vw	830 sh	
$\rho(NH_2)$		740 sh	775 sh	780 sh	780 sh		
	700 s		735 sh	745 sh	745 sh	550s(br)	1.32
		700 s	710 m	718 s	725 m		
ν(CrN)(en)	545 vs	534 sh	580 s	585 sh	580 s		

(continued overleaf)

TABLE IV. *(continued)*

	I	II	III	IV	V	Vb	ν(NH)/ν(ND)
	480 sh		538 s	535 sh	535 s		
		485 s	475 s	470 vs	470 s	550 br	
ring def.	545 vs	546 vs	550 sh	545 vs	545 s	550 br	
	330 sh			450–300 br	330 sh		
	125 m	130 m	125 m	120 m	120 m		
δ(CrNCCNCr)			510 sh		510 s	550 br	
			412 sh	510 sh			
				400 br	410 sh		
ν(NO)	1645 vs	1662 vs	1667 vs	1687 vs	1689 vs	1680 vs	
				1670 sh			
ν(CrN)(NO)	620 sh	615 sh	615 sh	620 sh	630 sh	632 sh	
δ(CrNO)	612 m	615 sh	615 sh	620 sh	615 sh	615 sh	
ν(CN)	2135 sh	2135 sh	2140 sh	450–300 br			
	2110 vs	2101 s	2100 m				
ν(CrC)	429 s	430 s	432 s				
	345 s	350 m	346 m				
δ(CrCN)	398 s	398 sh	398 s				
	293 w	295 w	298 w				

TABLE V. Experimental and Calculated EPR Parameters for the Chromium Nitrosyl complexes.

Compounds	g_o	$g_\perp$	$g_\parallel$	10^4 cm T_{zz} (±0.2)	10^4 cm K (±0.2)	c^2_{xy}	100 c^2_{2s}	100 c^2_{2p}	c^2_{2p}/c^2_{2s}
$[CrNO(CN)_5]^{3+}$	1.994	2.004	1.972	12.40	−16.80	0.75	0.92	5.34	5.80
$[CrNO(CN)_2(en)OH]^-$	1.994	2.003	1.975	15.46	−17.96	0.82	0.93	5.40	5.81
$[CrNO(CN)_2(en)(H_2O)]$	1.994	2.006	1.972	16.60	−18.68	0.95	0.94	5.64	6.00
$[Cr_2(NO)_2(CN)_4(en)_3]$	1.994	2.004	1.973	16.86	−18.19	0.97	0.93	5.70	6.13
$[Cr_2(NO)_2(CN)_2(en)_4]^{2+}$	1.994	2.005	1.973	–	–	–	0.94	–	–
	1.981		1.952	–	–	–	–	–	–
$[Cr_2(NO)_2(en)_5]^{4+}$	1.981	2.004	1.953	9.54	−21.94	0.49	–	–	–
$[CrNO(NH_3)_5]^{2+\,a}$	1.979	1.992	1.946	9.56	−22.74	0.52	0.94	–	–
$[CrNO(H_2O)_5]^{2+\,a}$	1.967	1.995	1.913	6.34	−19.79	0.25	0.97	6.80	7.01

[a] c^2_{xy}, c^2_{2p}, C^2_{2s} coefficients and the isotropic contact term K were calculated on the basis of experimental EPR parameters given by Goodman *et al.* [2]. The EPR spectra of the complexes I–VI were measured in formamide solutions.

tively (Table IV). The presence of the two ν(CN) and two ν(NO) frequencies in the IR spectrum of the complex (IV) is evidence of its dimeric structure (Table IV). Such a structure (Fig. 2b) was confirmed also by the analysis of the EPR and electronic absorption spectra which exhibit the bands characteristic of components of that dimer.

The CrNO and CrCN vibration frequencies in the IR spectra of the examined complexes appear in regions close to that of the pentacyanonitrosyl

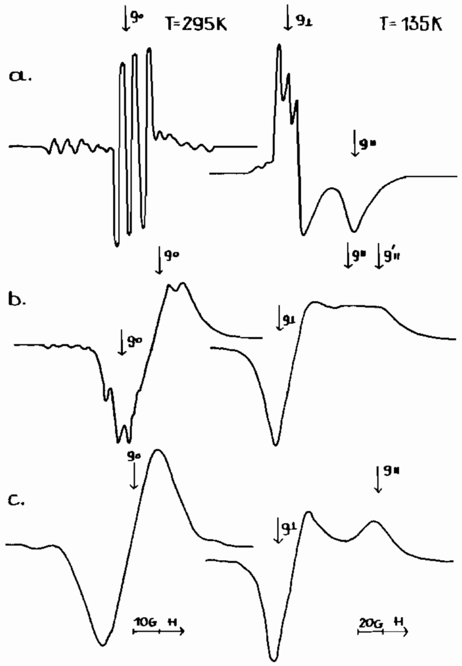

Fig. 3. EPR spectra of the chromium nitrosyl complexes: a, The typical spectrum for the complexes (I), (II), (III) and (VI) in formamide solution. b, Spectrum of the complex (IVa) in formamide solution. c, Spectrum of the complex (Va) in formamide solution.

compound [13, 14], which affords possibilities for their identification (Table IV).

ESR Spectra

In Fig. 3, the experimental EPR spectra for the investigated chromium nitrosyl complexes are given. The spectra of the chloride (V) and tetraphenylborate salt (Va) of the $[Cr_2(NO)_2(en)_5]^{4+}$ ion show no hyperfine structure. The spectrum of the solution of the tetraphenylborate salt of $[Cr_2(NO)_2(CN)_2\text{-}en)_4]^{2+}$ (IVa) (T = 295 K) consists of lines characteristic of the complexes III and V (Fig. 3).

Like in the spectrum of the frozen solution, two corresponding *g* values are observed. The character of this spectrum is therefore evidence for the structure assumed by us (Fig. 2b) and, furthermore, reveals lack of exchange interactions via the ethylenediamine bridge.

The spin Hamiltonian and bonding parameters obtained for the investigated complexes are given in Table V. The spin Hamiltonian parameters indicate that the unpaired electron occupies the molecular orbital $\psi = c_{xy}d_{xy} - c\phi_{lig}$. For such an electronic configuration, the c_{xy}^2 coefficient and the isotropic contact term K were calculated from the McGarvey relations [15]. For complexes in which the hyperfine interaction from ^{14}N (NO) was also observed, the $c_{2s}^2 = A_{iso}/A_{iso}^o$ and $c_{2p}^2 = T_{zz}/T_{zz}^o$ coefficients were calculated (A_{iso} = isotropic part of the hyperfine interaction; T_{zz} = component of the anisotropic hyperfine tensor) [16]. The sings of the hyperfine parameters for the investigated complexes were postulated upon the general properties of those parameters [15] and upon the zero-field spectroscopy investigations of similar complexes [17]. The $A_{iso}[^{14}N(NO)] < 0$ and $T_{zz}[^{14}N(NO)] > 0$ values are due to the negative spin density on the p_π orbital of the nitrosyl nitrogen because of the spin polarisation of the nitrogen containing π^* (NO) orbital through π ($d_{xz,yz}$ proper ligand-system) [18, 19].

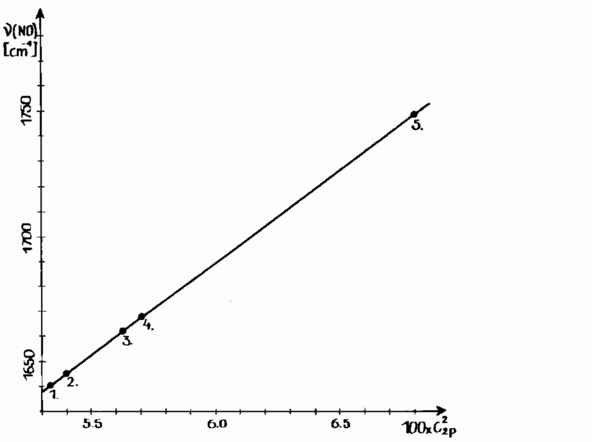

Fig. 4. The relationship between c_{2p}^2 and ν(NO) for the chromium nitrosyl complexes: 1, complex (VI); 2, complex (I); 3, complex (II); 4, complex (III); 5, $CrNO(H_2O)_5]^{2+}$.

Replacement of the CN^- ligands in the $[CrNO(CN)_5]^{3-}$ ion by ligands of different coordination abilities changes essentially the electron density distribution in the molecular unit {CrNO}. These changes are illustrated by the results compiled in Table V. The decreasing amount of the coordinated cyanate ligands causes an electron density increase on central atom and on the nitrosyl nitrogen due to the decreasing electron delocalization in the whole complex molecule.

The considerably lower c_{xy}^2 values in the case of the complex V and $[CrNO(NH_4)_5]^{2+}$ and $[CrNO(H_2O)_5]^{2+}$ (Table V) might be due to the different sequence of energetic levels (*e.g.* σ^* orbitals).

A strong dependence of the EPR parameters on the σ-donor ligands only has been found (compare complexes II, III and V and V, VII and VIII, Table V). The direction of the observed changes is consistent with the position of the ligands in the nephelo-auxetic series. The electron density increase on the nitrosyl nitrogen has a direct influence on the N–O bonding strength. This relationship is plotted in Fig. 4.

TABLE VI. Electronic Absorption Spectra of the Chromium Nitrosyl Complexes of $[CrNO(CN)_x(en)_y]^{n\pm}$ type.

$[CrNO(CN)_2(en)(OH)]^-$		$[Cr_2(NO)_2(CN)_2(en)_3]^{2+}$		$[Cr_2(NO)_2(en)_5]^{4+}$		$[CrNO(CN)_5]^{3-}$ [a]		Assignments[a]
$[cm^{-1}]$	ϵ max	$[cm^{-1}]$	ϵ max	$[cm^{-1}]$	ϵ max	$[cm^{-1}]$	ϵ max	
14300	9.1	17400(sh)	(31)	17800	33	13700	8	$^2B_2 \rightarrow {}^2E$ $(6e \rightarrow 2b_2)$
		13600(sh)	(3.9)	12600	1.9	15380	1.5	$\rightarrow {}^2E(2b_2 \rightarrow 7e)$
22250	116	22200	85	22000	79	22200	72	$\rightarrow {}^2B_2$ $(6e \rightarrow 7e)$
24800	128			27600	180	27320	59	$\rightarrow {}^2B_1$ $(2b_2 \rightarrow 3b_1)$
29700(sh)	(223)	30600(sh)	(273)					
36800	1560			32400	434	37300	1100	$\rightarrow {}^2E$ $(5e \rightarrow 2b_2)$
43350	5010	41500	2400	42050(sh)	(3400)	43480	3600	$\rightarrow {}^2E(2b_2 \rightarrow 8e)$
		44000(sh)	(3500)					

[a] Ref. 20, sh = shoulder.

Electronic Absorption Spectra

The structural changes observed in the investigated compounds are also reflected in their electronic absorption spectra (Table VI). The EPR spectra allowed to suggest the $^2B_2$ term being the ground term. In the series of complexes $[CrNO(CN)_5]^{3-}$, $[CrNO(CN)_2(en)(OH)]^-$ and $[CrNO(en)_{2,5}]^{2-}$ the decreasing π-interaction of ligands is accompanied first of all by the destabilization of the b_2 orbital, so that in the final substitute it becomes a non-bonding one. Therefore an energy increase of the $^2B_2 \rightarrow {}^2E$ $[e(d_{xz}, d_{yz} + \pi^*NO) \rightarrow b_2(d_{xy})]$ transition is observed, while the corresponding to the $^2B_2 \rightarrow {}^2E$ $[b_2(d_{xy}) \rightarrow e(\pi^*NO + d_{xz}, d_{yz})]$ transition is shifted downfield (Table VI).

The energy changes of the e levels, *i.e.* $(d_{xz}, d_{yz} + \pi^*NO)$ and $(\pi^*NO + d_{yz}, d_{xz})$, are parallel, and therefore the bands corresponding to transitions between them remain practically unchanged in the series of the $[CrNOL_5]^{n+}$ type complexes [2]. The σ^* orbitals and mainly $b_1(d_{x^2-y^2})$, also undergo destabilization. We suggest the following sequence of the molecular orbitals for the complex $[(en)_2ONCr(en)CrNO(en)_2]^{4+}$ (C_{4v} symmetry): $e(d_{xy}, d_{yz} + \pi^*NO)^4 < b_2(d_{xy})^1 < e(\pi^*NO + d_{xz}, d_{yz}) < a_1(d_{z^2}) < b_1(d_{x^2-y^2})$. Thus, the σ^* orbital sequence is reverse to that proposed *e.g.* by Manoharan and Gray [20] or Fenske [21] for the $[CrNO(CN)_5]^{3-}$ ion. Comparable σ-donor properties of ethylenediamine and NH_3 allows one to suppose that in the complex $[Cr_2(NO_2(en)_5]^{4+}$ the b_1 level may be raised over the a_1 one, as it was proved for the $[CrNO(NH_3)_5]^{3+}$ complex [2].

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