Synthesis and study of the novel tri-nuclear 5-thio(seleno)pyrazolealdiminato bis-chelates containing a η^6-arenechromiumtricarbonyl moiety

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Abstract

Novel 4-aminomethylene-5-thio(seleno)pyrazoles containing an η^6-coordinated $Cr(CO)_3$ moiety have been prepared and used as ligands for the synthesis of tetrahedral Zn^{II}, Cd^{II}, Hg^{II} and Ni^{II} tri-nuclear metal-chelates studied by means of ^1H NMR, IR spectroscopy and magnetic susceptibility determination. An X-ray investigation of the bis(1-phenyl-3-methyl-4-phenylchromiumtricarbonylaldimino-5-thionato) Ni^{II} complex has been undertaken. A pseudo-tetrahedral bond configuration of the nickel atom has been revealed with metal–ligand bond lengths as follows: Ni–N 2.02(2); 1.95(2) Å; Ni–S 2.257(6); 2.223(7) Å. The interatomic distances Ni $\cdots$ Cr of 5.04 and 5.07 Å show no metal–metal interactions. The structural parameters of the π-coordinated $Cr(CO)_3$ moiety are similar to those of the typical phenylchromiumtricarbonyl derivatives.
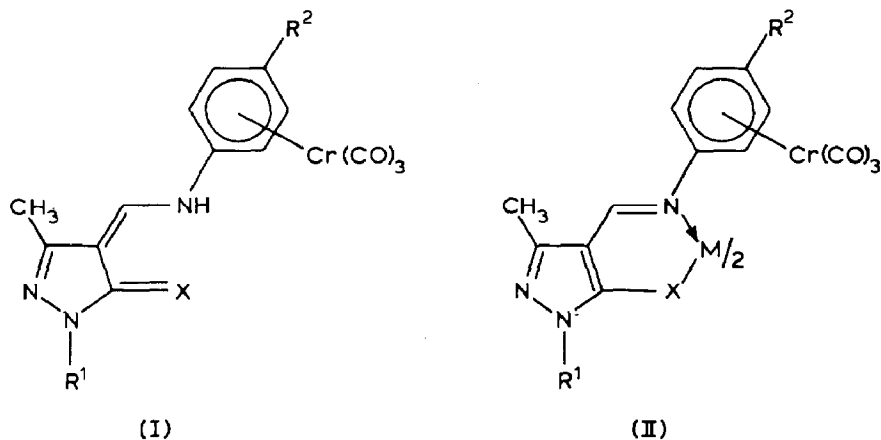
Introduction

Metal carbonyls are known to produce complexes of differing structure under reactions with Schiff bases. A variety of studies on the reactions, giving σ-complexes, ortho-metallated species, and clusters, have appeared [1–5]. The Schiff bases containing a π-bonded organometallic moiety have been less extensively studied. Such species as well as β-dikethonate metal carbonyl derivatives [6] and N-ferrocenyl-2-hydroxybenzylideneimines [7] are of importance as potential ligands to be utilized for the synthesis of di- and poly-nuclear chelate compounds.

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So far only one communication [8] has been published on the isolation of similar Schiff base complexes of η^6-ArCr(CO)$_3$-coordinated salicylaldimines. However, the structures identified there seem to be problematical since the authors interpreted the elemental analysis data as representing a single molecule of the complex containing up to 13 molecules of water.

Results and discussion

We have prepared the novel 1,3-substituted 4-arenechromiumtricarbonyla-minomethylene-5-thio(seleno)pyrazoles. Unlike the η^6-ArCr(CO)$_3$-coordinated phenylaldimines [4] which are obtained under rigorous conditions by reaction of Cr(CO)$_6$ with the Schiff base at 150–160°C in a heptane-diglyme mixture, the anlogous pyrazole derivatives have been prepared under mild conditions by condensation of η^6-C$_6$H$_5$NH$_2$Cr(CO)$_3$ or η^6-CH$_3$-p-C$_6$H$_4$NH$_2$Cr(CO)$_3$ and corresponding aldehydes at room temperature in high yields. Elemental analysis, IR, and NMR spectroscopy indicate that their structures are as depicted (I):

(I)   (II)

R$_1$ = Ph (I, IIa *), i-Pr (I, IIb); R$_2$ = H, CH$_3$; X = S, Se; M = Zn^{II}, Cd^{II}, Ni^{II}, Hg^{II}.

In the IR spectra of I in CHCl$_3$, the CO groups exhibit two stretching bands in the region 1890–1990 cm^{-1} unique to a Cr(CO)$_3$ moiety with C_{3v} symmetry. The absorbtion bands of the primary amino group at 3490 and 3400 cm^{-1} from the initial η^6-C$_6$H$_5$NH$_2$Cr(CO)$_3$ are not observed. In the ^{1}H NMR spectra of I the proton signal of π-coordinated arene rings, δ 4.9–5.8 ppm, are shifted upfield by 1.5–2.0 ppm similar to the analogous π-complexes. The aminomethylene structure of I with a strong intramolecular hydrogen bond is confirmed by the NH-proton doublet signals ^3J(CH–NH) 11–12 Hz, δ 14.0–14.8 ppm, shifted slightly upfield by 0.3–0.4 ppm as compared with those in non-coordinated compounds [9], which appears to be related to the acceptor properties of the Cr(CO)$_3$ substituent.

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* For a preliminary communication on the preparation and study of ligands and complexes I, IIa (see ref. 10).

Table 1

Elemental analysis and IR spectroscopy data of I, II [a]

Entry	X	R_1	R_2	M	Anal. (found (calc) (%))			ν(CO) cm^{-1}
					C	H	N	
1	S	C_6H_5	H		56.0 (55.9)	3.6 (3.5)	9.8 (9.8)	1986, 1920
2	Se	C_6H_5	H		50.4 (50.4)	3.2 (3.2)	8.8 (8.8)	1988, 1920
3	S	C_6H_5	CH_3		56.5 (56.9)	3.8 (3.9)	9.5 (9.5)	1981, 1914
4	S	C_3H_7	H		52.0 (51.6)	4.8 (4.3)	10.3 (10.6)	1986, 1919
5	Se	C_3H_7	H		46.0 (46.2)	3.6 (3.9)	9.1 (9.5)	1986, 1919
6	S	C_3H_7	CH_3		52.2 (52.8)	4.2 (4.7)	10.1 (10.3)	1980, 1899
7	S	C_6H_5	H	Ni	52.4 (52.5)	3.1 (3.1)	9.2 (9.2)	1973, 1912, 1901 (sh)
8	Se	C_6H_5	H	Ni	47.6 (47.6)	3.0 (2.8)	8.3 (8.3)	1976, 1918, 1880 (sh)
9	S	C_3H_7	H	Ni	47.9 (48.2)	3.2 (3.8)	9.6 (9.9)	1976, 1916, 1902 (sh)
10	Se	C_3H_7	H	Ni	43.0 (43.4)	3.7 (3.4)	8.6 (8.9)	1977, 1917, 1901 (sh)
11	S	C_3H_7	CH_3	Ni	49.1 (49.4)	3.9 (4.1)	9.2 (9.6)	1972, 1912, 1898 (sh)
12	S	C_6H_5	H	Zn	52.0 (52.1)	3.1 (3.1)	9.1 (9.1)	1983, 1915, 1903 (sh)
13	S	C_6H_5	H	Cd	49.3 (49.6)	3.0 (2.9)	8.7 (8.7)	1980, 1910, 1900 (sh)
14	S	C_6H_5	CH_3	Hg	46.4 (46.5)	2.9 (3.0)	7.5 (7.7)	1973, 1903, 1891 (sh)
15	Se	C_6H_5	H	Zn	47.0 (47.3)	2.7 (2.8)	8.0 (8.3)	1979, 1913, 1900 (sh)
16	Se	C_6H_5	H	Cd	45.0 (45.2)	2.8 (2.7)	8.0 (7.9)	1977, 1911, 1900 (sh)
17	Se	C_6H_5	H	Hg	41.5 (41.7)	3.0 (2.5)	7.4 (7.3)	1975, 1908, 1895 (sh)
18	S	C_3H_7	H	Zn	48.0 (47.8)	4.0 (3.8)	10.2 (9.8)	1978, 1911, 1902 (sh)
19	S	C_3H_7	H	Cd	45.1 (45.3)	3.9 (3.6)	9.9 (9.3)	1977, 1909, 1903 (sh)
20	S	C_3H_7	H	Hg	41.2 (41.3)	3.5 (3.3)	8.3 (8.5)	1974, 1904, 1897 (sh)
21	Se	C_3H_7	H	Zn	43.6 (43.1)	3.6 (3.4)	8.5 (8.9)	1979, 1913, 1901 (sh)
22	Se	C_3H_7	H	Cd	40.9 (41.1)	3.1 (3.2)	8.2 (8.5)	1977, 1910, 1901 sh)
23	S	C_3H_7	CH_3	Zn	48.8 (49.0)	4.2 (4.1)	9.0 (9.5)	1973, 1906, 1899 (sh)
24	O	C_6H_5	H		58.2 (58.0)	3.7 (3.7)	10.4 (10.2)	1981, 1918
25	O	C_6H_5	H	Zn	53.9 (54.0)	3.3 (3.1)	9.4 (9.5)	1982, 1911, 1873 (sh)

[a] Entries 1–6 represent complexes of type I, entries 7–23, 25 those of type II.

Table 2

^{1}H NMR chemical shifts for the Ni^{II} complexes IIa, IIb (20 °C, CDCl$_3$)

Entry [a]	δ (ppm)								
	o-H	m-H	p-H	o'-H [b]	m'-H	p'-H	CH$_3$	(CH$_3$)$_2$CH	CH(CH$_3$)$_2$
7	19.04	6.86	9.57	1.10	17.26	4.21	−15.06	–	–
8	18.57	6.32	9.49	1.25	15.70	3.90	−11.88	–	–
9	–	–	–	1.40	16.92	4.10	−14.65	3.69	−0.75
10	–	–	–	1.13	15.99	3.92	−13.36	4.29	−2.72
11	–	–	–	1.60	16.41	7.39 [c]	−14.14	3.85	−0.85

[a] Numbering is as in Table 1. [b] Primes denote coordinated aryl ring protons. [c] p'-CH$_3$.

Reaction of I with metal acetates in ethanol solution gives the tri-nuclear Zn^{II}, Cd^{II}, Hg^{II}, and Ni^{II} metal-chelates of type II. The IR spectra of II (Table 1) show an extra shoulder on the CO E$_1$ absorption, as compared with that of I. In the NMR spectra of II the NH-proton signals of the starting imine, I, disappear whereas the CH=N signal, δ 8.1–8.4 ppm, becomes a singlet.

The Ni^{II} complexes II are paramagnetic tetrahedral species in solution. Their ^{1}H NMR contact shifts are not concentration-dependent in the accessible range of 1×10^{-2}–5×10^{-3} mol/l (Table 2), while a linear contact shifts vs. $1/T$ dependence was observed in accordance with the Curie law (see Experimental). Assignments of the signals were made on the basis of previously published data [11,12]. The magnetic moments of the Ni^{II} complexes in solution and in the solid state (Table 3) lie within 3.0–3.6 BM which is characteristic of the tetrahedral Ni^{II} complexes with a strong spin-orbital interaction.

The nickel atom in complex IIa (X = S, R$_2$ = H) possesses a slightly cis-distorted pseudo-tetrahedral bond configuration, as determined from X-ray diffraction. The structure of the molecule is shown in Fig. 1, bond lengths and bond angles are listed in Tables 4 and 5. The angle between the NiN(1)S(1) and NiN(4)S(2) plane is equal to 86.5°, in accord with the magnetic moment in the solid state, viz., 3.3 BM. The bonds to the Ni atom are: Ni–S(1) 2.257(6); Ni–S(2) 2.223(7); Ni–N(1) 2.02(2); Ni–N(2) 1.95(2) Å. The nickel valence angles lie between 100–126°. Both the

Table 3

The magnetic moments, free activation energies, and rate constants at coalescence temperature for $R \rightleftharpoons S$ interconversion in the Ni^{II} complexes IIa, IIb

Entry [a]	Indicator group	T_C (K)	$\Delta \nu_{1/2}$ [b] (Hz)	$\Delta G^{\neq} (T_C)$ (kJ/mol)	k (s^{-1} ×10^{-2})	μ_{eff} (BM) (CHCl$_3$)	μ_{eff}, (BM) (solid state)
7	m'-H	243	105	48.1	2.33	3.6	3.3
8	m'-H	253	75	50.8	1.67	3.1	3.6
9	i-Pr	258	50	52.7	1.11	3.0	3.4
	m'-H	263	105	52.2	2.32		
10	i-Pr	283	120	56.0	2.66	3.2	3.1
	m'-H	273	50	55.9	1.11		
11	i-Pr	253	145	49.4	3.22	3.3	3.3
	m'-H	233	25	48.8	0.555		

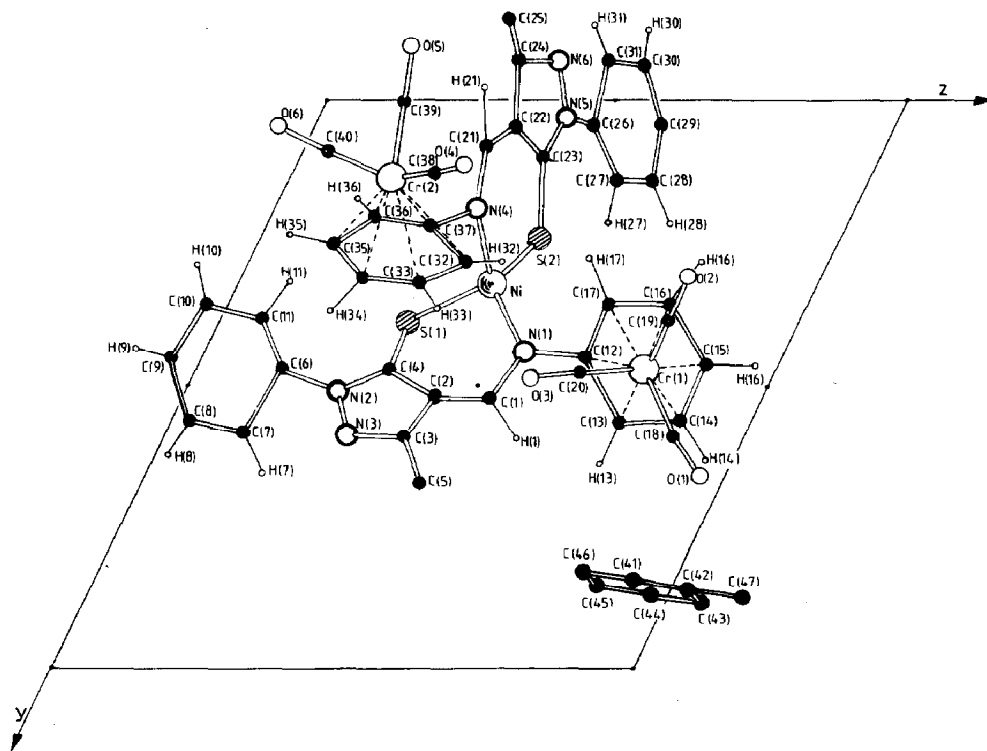[a] Numbering is as in Table 1. [b] Linewidths at half height for indicator group signals.

Fig. 1. The structure of the nickel complex IIa (X = S, R^2 = H).

former and the latter values are typical of NiN_2S_2 bis-chelates [13–15].The Cr(1)NiCr(2) unit has a nonlinear structure with an 84° bend. The interatomic distances Ni $\cdots$ Cr(1), 5.04 Å, and Ni $\cdots$ Cr(2), 5.07 Å, exceed the sum of the Ni and Cr van der Waals radii, which indicates that there are no shortened Ni $\cdots$ Cr contacts and thus no metal–metal interactions.

One of the metallocycles NiN(1)C(21)C(22)C(23)S(2) is practically planar while the second ring NiN(1)C(1)C(2)C(4)S(1) is folded along the N(1)–S(1) axis at 20°. Pyrazole rings are planar to within 0.03 Å. The phenyl groups attached to the pyrazole rings and bonded to the coordinated nitrogen, are rotated by 12° (N(2)–Ph), 38° (N(5)–Ph), 96° ((N(4)–Ph), 53° (N(1)–Ph) (relative to the N(1)C(1)C(2)C(4)S(1) plane).

The bond lengths of the coordinated phenyl rings lie in the range of 1.35–1.46 Å. The mean value of the Cr–C_{Ph} distance is 2.24 Å, Cr–C_{carb} 1.86 Å, C–O 1.16 Å. The chromium atoms are oriented so as to face the center of the benzene rings. The $Cr(1)(CO)_3$ moiety has eclipsed conformation relative to the benzene ring, but $Cr(2)(CO)_3$ is skewed by 10°.

The electronic structure of the coordinated ligand corresponds to the delocalized iminothiolato form. The values of bond lengths in chelate rings are similar to those previously reported for analogous bis(pyrazolealdiminato) Ni^{II} complexes [13].

The tetrahedral Ni^{II} complexes of type II exist as R and S enantiomers that are the spacial isomers with differing environment at the nickel center. The most plausible mechanism operative in the R ⇌ S interconversion that proceeds readily in solution, is diagonal twist rearrangement. The activation energies of the process

Table 4

Bond lengths (Å)

Ni–S(1)	2.257(6)	N(6)–C(24)	1.33(3)
Ni–S(2)	2.223(7)	C(1)–C(2)	1.39(3)
Ni–N(1)	2.02(2)	C(2)–C(3)	1.42(3)
Ni–N(2)	1.95(2)	C(2)–C(4)	1.44(3)
Ni–Cr(1)	5.04(2)	C(3)–C(5)	1.50(3)
Ni–Cr(2)	5.07(2)	C(6)–C(7)	1.39(3)
Cr(1)–C(12)	2.30(2)	C(6)–C(11)	1.36(3)
Cr(1)–C(13)	2.26(2)	C(7)–C(8)	1.44(3)
Cr(1)–C(14)	2.21(2)	C(8)–C(9)	1.38(3)
Cr(1)–C(15)	2.19(2)	C(9)–C(10)	1.35(4)
Cr(1)–C(16)	2.23(2)	C(10)–C(11)	1.38(3)
Cr(1)–C(17)	2.29(2)	C(12)–C(13)	1.40(3)
Cr(1)–C(18)	1.84(3)	C(12)–C(17)	1.43(3)
Cr(1)–C(19)	1.85(3)	C(13)–C(14)	1.42(3)
Cr(1)–C(20)	1.83(2)	C(14)–C(15)	1.39(3)
Cr(2)–C(32)	2.26(2)	C(15)–C(16)	1.42(3)
Cr(2)–C(33)	2.21(3)	C(16)–C(17)	1.46(3)
Cr(2)–C(34)	2.20(3)	C(18)–O(1)	1.19(3)
Cr(2)–C(35)	2.22(3)	C(19)–O(2)	1.14(4)
Cr(2)–C(36)	2.25(2)	C(20)–O(3)	1.16(3)
Cr(2)–C(37)	2.27(2)	C(21)–C(22)	1.43(3)
Cr(2)–C(38)	1.90(3)	C(22)–C(23)	1.39(3)
Cr(2)–C(39)	1.83(3)	C(22)–C(24)	1.42(3)
Cr(2)–C(40)	1.82(3)	C(24)–C(25)	1.54(3)
S(1)–C(4)	1.72(3)	C(26)–C(27)	1.37(4)
S(2)–C(23)	1.74(3)	C(26)–C(31)	1.42(3)
N(1)–C(1)	1.31(3)	C(27)–C(28)	1.41(4)
N(1)–C(12)	1.44(2)	C(28)–C(29)	1.38(4)
N(2)–N(3)	1.42(3)	C(29)–C(30)	1.34(4)
N(2)–N(4)	1.38(3)	C(30)–C(31)	1.41(4)
N(2)–N(6)	1.46(3)	C(32)–C(33)	1.45(4)
N(3)–C(3)	1.34(3)	C(32)–C(37)	1.41(3)
N(4)–C(21)	1.30(3)	C(33)–C(34)	1.35(3)
N(4)–C(37)	1.42(3)	C(34)–C(35)	1.46(4)
N(5)–N(6)	1.40(3)	C(35)–C(36)	1.42(4)
N(5)–C(23)	1.35(3)	C(36)–C(37)	1.46(3)
N(5)–C(26)	1.43(3)	C(38)–O(4)	1.14(4)
C(41)–C(42)	1.33(5)	C(39)–O(5)	1.17(4)
C(41)–C(46)	1.52(5)	C(40)–O(6)	1.17(3)
C(42)–C(43)	1.47(6)		
C(42)–C(47)	1.51(6)		
C(43)–C(44)	1.43(5)		
C(44)–C(45)	1.47(4)		
C(45)–C(46)	1.39(6)		

measured by ^{1}H NMR spectroscopy, when observing the dynamic behaviour of diastereotopic methyl groups or methylene protons of the benzyl group for the bis(pyrazolealdiminato) Ni^{II} complexes not carrying a $Cr(CO)_3$ substituent, lie in the range of 40–75 kJ/mol [11]. Similarly, $R \rightleftharpoons S$ interconversion has also been found to occur in complexes II. The typical temperature-dependent spectral patterns are shown in Fig. 2. The rate constants and free activation energies obtained by a

Table 5

Bond angles (°)

S(1)NiS(2)	117.6(2)	C(6)C(7)C(8)	116.4(20)
S(1)NiN(1)	100.4(5)	C(7)C(8)C(9)	121.3(22)
S(1)NiN(4)	105.2(5)	C(8)C(9)C(10)	118.8(24)
S(2)NiN(1)	126.5(5)	C(9)C(10)C(11)	121.9(23)
S(2)NiN(4)	100.2(5)	C(6)C(11)C(10)	120.2(22)
N(1)NiN(4)	104.6(6)	Cr(1)C(18)O(1)	178.6(22)
NiS(1)C(4)	102.1(8)	Cr(1)C(19)O(2)	178.9(24)
NiS(2)C(23)	105.8(7)	Cr(1)C(20)O(3)	175.1(21)
NiN(1)C(1)	125.0(14)	N(4)C(21)C(22)	124.9(19)
NiN(1)C(12)	116.3(12)	C(21)C(22)C(23)	128.9(20)
N(3)N(2)C(4)	110.1(16)	C(23)C(22)C(24)	105.8(19)
N(3)N(2)C(6)	118.5(16)	S(2)C(23)N(5)	123.8(15)
C(4)N(2)C(6)	131.4(18)	S(2)C(23)C(22)	129.7(16)
N(2)N(3)C(3)	107.5(17)	N(5)C(23)C(22)	106.5(17)
NiN(4)C(21)	130.4(14)	N(6)C(24)C(22)	110.9(20)
NiN(4)C(37)	111.9(13)	N(6)C(24)C(25)	120.8(20)
C(21)N(4)C(37)	117.2(17)	C(22)C(24)C(25)	128.3(20)
N(6)N(5)C(23)	112.1(16)	N(5)C(26)C(27)	121.4(21)
N(6)N(5)C(26)	114.4(16)	N(5)C(26)C(31)	118.3(20)
C(23)N(5)C(26)	133.3(18)	C(27)C(26)C(31)	120.2(21)
N(5)N(6)C(24)	104.7(17)	C(26)C(27)C(28)	119.7(25)
N(1)C(1)C(2)	128.8(19)	C(27)C(28)C(29)	119.3(27)
C(1)C(2)C(3)	126.9(19)	C(28)C(29)C(30)	121.6(28)
C(1)C(2)C(4)	126.8(19)	C(29)C(30)C(31)	120.8(28)
C(3)C(2)C(4)	107.2(18)	C(26)C(31)C(30)	118.3(25)
N(3)C(3)C(2)	109.5(19)	Cr(2)C(38)O(4)	175.1(28)
N(3)C(3)C(5)	121.9(19)	Cr(2)C(39)O(5)	174.9(23)
C(2)C(3)C(5)	128.5(19)	Cr(2)C(40)O(6)	177.3(24)
S(1)C(4)N(2)	122.6(16)	C(42)C(41)C(46)	123.9(30)
S(1)C(4)C(2)	131.6(17)	C(41)C(42)C(43)	130.7(34)
N(2)C(4)C(2)	105.6(18)	C(41)C(42)C(47)	129.5(34)
N(2)C(6)C(7)	115.7(19)	C(43)C(42)C(47)	99.8(32)
N(2)C(6)C(11)	122.9(20)	C(42)C(43)C(44)	101.3(31)
C(7)C(6)C(11)	121.4(21)	C(43)C(44)C(45)	134.1(31)
C(44)C(45)C(46)	119.1(31)	C(16)C(17)C(12)	117.2(20)
C(41)C(46)C(45)	110.8(34)	N(4)C(37)C(32)	119.4(20)
N(1)C(12)C(13)	122.7(18)	N(4)C(37)C(36)	117.3(20)
N(1)C(12)C(17)	116.5(17)	C(32)C(37)C(36)	122.6(20)
C(13)C(12)C(17)	120.7(18)	C(37)C(32)C(33)	117.0(21)
C(12)C(13)C(14)	121.5(18)	C(32)C(33)C(34)	120.9(22)
C(13)C(14)C(15)	119.2(18)	C(33)C(34)C(35)	120.9(23)
C(14)C(15)C(16)	121.1(20)	C(34)C(35)C(36)	117.3(23)
C(15)C(16)C(17)	120.3(20)	C(35)C(36)C(37)	118.5(20)

coalescence study are given in Table 2. Noteworthy an are the higher $\Delta G^{\neq}(T_c)$ values (by 5–10 kJ/mol) as for the complexes in which a $Cr(CO)_3$ substituent is present. Similar to the species not having a $Cr(CO)_3$ substituent, the activation energies for II increase on going from X = S to X = Se.

The dynamic ^1H NMR spectra of Ni^{II} complexes II, revealed the unusual behaviour of the η^6-ArCr(CO)$_3$ meta-proton signals, which was not observed when a conventional aryl substituent is attached to the coordinated nitrogen. Their low

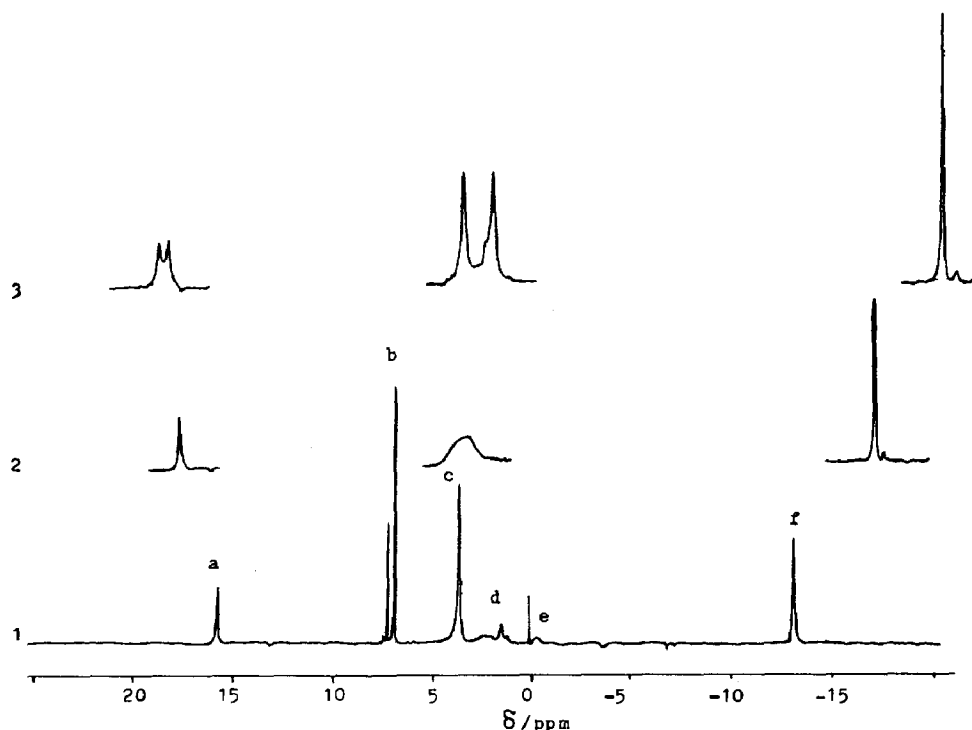Fig. 2. The ^{1}H NMR temperature-dependent spectra of the nickel complex IIb (X = S, R$_2$ = CH$_3$) in CDCl$_3$: (1) At T 20 °C (a–m'–H, b–p'-CH$_3$, c–(CH$_3$)$_2$, d–o'-H, e–CH(i-Pr), f–CH$_3$); (2) at T −20 °C; (3) at T −45 °C.

temperature (−10 to −50 °C) spectra consist of two singlet signals perturbed by paramagnetic broadening. These signals coalesce upon warming. The observed spectral behaviour is probably because the Cr(CO)$_3$ moiety induces an increased difference in the chemical shifts of the m-protons which have different environments. The $R \rightleftharpoons S$ interconversion of bis(aminovinylthionato) Zn^{II} complex has been similarly studied by monitoring the coalescence of the mesitylene o-methyl signals [16]. It should be pointed out that activation parameters obtained by use of the various indicator groups (Table 3) are very similar.

On the other hand, there may be an alternative consideration, viz., that the steric constraints offered by the Cr(CO)$_3$ moiety result in hindered rotation of the η^6-ArCr(CO)$_3$ group about the C–N axis. High field dynamic ^{13}C NMR studies of the isoligand Zn^{II} complexes are being conducted to determine whether the two different mechanisms do operate and whether they take place at differing rates.

The ^{1}H NMR spectral patterns of the Zn^{II} complexes of type II show too small a degree of diastereotopic splitting of the isopropyl methyls (1–2 Hz) to carry out a full line shape analysis and to determine th kinetic and the activation parameters of the enantiomerization. The behaviour observed for the Zn^{II} as well as that of the Cd^{II} and Hg^{II}, complexes II resembles that of other bis(pyrazolealdiminato) metal-chelates containing aryl substituents at the coordinated nitrogen [10].

Finally, the unknown complexes, IIa, with X = O; M = Zn, Ni have also been prepared (Table 1) and will be discussed in a forthcoming paper [17].

Experimental

Synthesis

1,3-substituted 4-arenechromiumtricarbonylaminomethylene-5-thio(seleno)pyrazoles (Ia, Ib). A 0.01-*M* solution of η^6-$C_6H_5NH_2Cr(CO)_3$ prepared from aniline and $Cr(CO)_6$, as has been described previously [18], in 5 ml of ethanol was added to an ethanol (X = Se) or ether (X = S) solution containing 0.01 *M* 1-phenyl-3-methyl-4-formyl-5-thio(seleno)pyrazole, prepared in situ as has previously been described. After 15 min stirring at room temperature the precipitate that separated was filtered off, washed with ether, and purified by crystallization from ethanol. Yield of Ia 80–90%.

The enamines Ib (X = Se) were obtained as described above using 1-isopropyl-3-methyl-4-formyl-5-selenopyrazole [19].

In the case of Ib (X = S), equimolar amounts of η^6-$C_6H_5NH_2Cr(CO)_3$ or η^6-CH_3-$pC_6H_4Cr(CO)_3$ in ethanol solution were added to an aqueous solution of aldehyde [19] and the mixture was allowed to stand overnight. The crystals that formed were filtered off, and washed with water. Yield 70–80%.

Ia, Ib are stable red powders or crystals that slowly decompose on standing in air. Elemental data are listed in Table 1.

Metal-chelates IIa, IIb. The metal acetate and the appropriate enamine Ia, Ib (1 : 2) were refluxed in ethanol for 5 min. The complexes were filtered of and crystallized from toluene. Yield 80–90%. Characteristics are given in Table 1.

Spectral measurements. IR spectra were recorded on UR-20 and Specord-75 IR spectrometers in $CHCl_3$ solution, ^1H NMR spectra – on Tesla BS-567A and Varian XL-100/15 spectrometers (f 100 MHz) using HMDS as internal standard. Temperature was controlled to within $\pm 1°C$. The rate constants at coalescence temperatures were calculated by use of the standard equation $k(T_c) = \pi/\sqrt{2}\,\Delta\nu_{1/2}$, where $\Delta\nu_{1/2}$ is the linewidth at half height for the indicator group signals.

The magnetic moments for the complexes in solution were determined by Evans' method, and those for the solid state were determined by Faraday's technique.

Ia, Ib. ^1H NMR (δ, ppm, $CDCl_3$): 1.34–1.38 (d, 6H, $(CH_3)_2$, $^3J(CH_3–CH)$ 6.5–7.0 Hz); 2.24–2.34 (s, 3H, CH_3); 4.94–5.76 (m, 6H, C_6H_5 coord, CH (i-Pr)); 7.04–8.35 (m, 5H, $Npyr$-C_6H_5); 8.10–8.31 (d, 1H, CH–N, $^3J(CH–NH)$ 11–12 Hz); 14.05–14.76 (d, 1H, NH–C, $^3J(NH–CH)$ 11–12 Hz).

Diamagnetic complexes IIa, IIb. ^1H NMR (δ, ppm, $CDCl_3$): IIa,b: 1.32–1.47 (d, 12H, $2(CH_3)_2$); 2.20–2.54 (s, 6H, $2CH_3$); 4.81–5.62 (m, 12H, $2C_6H_5$(coord), 2CH(i-Pr)); 7.07–8.00 (m, 10H, $2Npyr$-C_6H_5); 8.12–8.41 (s, 2H, 2CH=N).

The chemical shifts for nickel complexes, are given in Table 2. The temperature-dependent contact shifts of the m'-H protons are best described as the linear equations: $y = 342000 \cdot 1/T + 544$ (Entry 7, Table 1, *T* in K), $y = 241213 \cdot 1/T + 253$ (Entry 8), $y = 430331 \cdot 1/T - 491$ (Entry 9), $y = 362505 \cdot 1/T + 352$ (Entry 10), $y = 361669 \cdot 1/(T - 289)$ (Entry 11). The isopropyl methyl signals show only a slight drift in the spectra (ca. 0.2–0.3 Hz/grad). Of the other signals, most of the changes are observed for the CH_3 protons: $y = -583054 \cdot 1/T + 525$ (Entry 7), $y = -346578 \cdot 1/T - 241$ (Entry 8), $y = -623705/T + 430$ (Entry 9), $y = -512175 \cdot 1/T + 192$ (Entry 10), $y = -534958 \cdot 1/T + 128$ (Entry 11).

X-ray diffraction study. The crystal was obtained by slow recrystallization from a toluene-heptane mixture.

Table 6

Atomic coordinates

Atom	x	y	z	$B^{eq.\ iso}$, B^{iso} (Å^2)
Ni	0.0283(2)	0.3226(2)	0.4417(2)	3.0
Cr(1)	0.4133(3)	0.4682(3)	0.7695(3)	3.4
Cr(2)	0.2009(3)	0.1463(3)	0.1856(3)	4.1
S(1)	−0.0461(4)	0.3865(4)	0.3223(4)	3.7
S(2)	−0.0819(5)	0.2433(4)	0.4894(4)	4.8
N(1)	0.1784(11)	0.4432(11)	0.5523(12)	3.0
N(2)	0.0662(13)	0.5120(11)	0.2676(13)	3.1
N(3)	0.1715(14)	0.5875(12)	0.3098(14)	3.6
N(4)	0.0588(12)	0.1956(12)	0.3500(12)	3.3
N(5)	−0.1528(12)	0.0297(13)	0.4366(13)	3.3
N(6)	−0.1521(13)	−0.0757(12)	0.3729(13)	4.3
O(1)	0.6346(13)	0.6525(12)	0.9444(12)	5.8
O(2)	0.5344(14)	0.3093(14)	0.7686(18)	9.9
O(3)	0.4711(12)	0.4834(14)	0.5930(13)	7.3
O(4)	0.4213(14)	0.1150(16)	0.2757(16)	8.7
O(5)	0.0997(15)	−0.0887(13)	0.1166(15)	8.0
O(6)	0.1773(14)	0.0495(14)	−0.0541(13)	7.7
C(1)	0.2235(14)	0.5152(14)	0.5318(14)	3.3
C(2)	0.1801(16)	0.5286(15)	0.4358(15)	2.7
C(3)	0.2382(17)	0.5989(15)	0.4118(17)	3.8
C(4)	0.0692(16)	0.4734(14)	0.3423(17)	4.7
C(5)	0.3577(15)	0.6725(14)	0.4810(15)	3.3
C(6)	−0.0233(16)	0.4880(16)	0.1589(17)	3.7
C(7)	−0.0247(15)	0.5764(14)	0.1406(15)	4.0
C(8)	−0.1109(18)	0.5538(16)	0.0322(18)	5.5
C(9)	−0.1872(17)	0.4489(17)	−0.0489(17)	5.6
C(10)	−0.1795(17)	0.3666(16)	−0.0258(17)	5.4
C(11)	−0.0993(16)	0.3851(16)	0.0776(17)	4.4
C(12)	0.2348(14)	0.4530(14)	0.6644(15)	2.9
C(13)	0.2878(14)	0.5546(13)	0.7680(15)	2.9
C(14)	0.3415(14)	0.5615(14)	0.8773(15)	4.0
C(15)	0.3392(15)	0.4649(15)	0.8810(16)	4.4
C(16)	0.2862(15)	0.3602(15)	0.7780(16)	4.1
C(17)	0.2328(14)	0.3522(13)	0.6651(14)	3.1
C(18)	0.5473(18)	0.5805(17)	0.8768(17)	4.8
C(19)	0.4878(18)	0.3700(17)	0.7698(20)	3.1
C(20)	0.4448(15)	0.4732(16)	0.6573(18)	4.4
C(21)	0.0222(14)	0.0926(16)	0.3200(18)	3.7
C(22)	−0.0482(15)	0.0496(15)	0.3567(14)	3.3
C(23)	−0.0932(14)	0.1055(13)	0.4264(15)	2.6
C(24)	−0.0886(19)	−0.0622(20)	0.3253(19)	4.3
C(25)	−0.0672(15)	−0.1605(15)	0.2471(16)	4.4
C(26)	−0.2210(16)	0.0342(17)	0.4925(17)	4.0
C(27)	−0.2146(19)	0.1329(18)	0.5753(20)	6.8
C(28)	−0.2825(21)	0.1345(20)	0.6294(20)	7.6
C(29)	−0.3515(19)	0.0352(20)	0.6010(20)	7.4
C(30)	−0.3585(20)	−0.0623(20)	0.5219(21)	8.3
C(31)	−0.2921(21)	−0.0667(19)	0.4650(20)	7.7
C(32)	0.2355(16)	0.2762(14)	0.3641(16)	4.6
C(33)	0.2908(18)	0.3237(16)	0.3167(18)	6.0
C(34)	0.2331(18)	0.3137(16)	0.2119(18)	6.0
C(35)	0.1154(17)	0.2524(16)	0.1379(17)	5.5

Table 6 (continued)

Atom	x	y	z	$B^{eq.iso}$, B^{iso} (Å^2)
C(36)	0.0582(15)	0.2059(14)	0.1821(15)	4.2
C(37)	0.1202(16)	0.2216(14)	0.2976(16)	3.7
C(38)	0.3395(21)	0.1294(19)	0.2469(23)	7.1
C(39)	0.1374(17)	0.0044(20)	0.1475(18)	4.4
C(40)	0.1889(18)	0.0870(17)	0.0404(19)	4.5
C(41)	0.4948(21)	0.8512(19)	0.9413(23)	7.6
C(42)	0.4976(29)	0.8679(25)	1.0421(29)	9.8
C(43)	0.4098(29)	0.8760(25)	1.0768(28)	11.7
C(44)	0.3228(22)	0.8644(20)	0.9799(25)	7.7
C(45)	0.3085(26)	0.8470(24)	0.8665(27)	9.5
C(46)	0.3976(26)	0.8438(22)	0.8433(25)	9.6
C(47)	0.5924(23)	0.8824(29)	1.1468(33)	14.1

The unit cell contains solvated toluene. Crystal, triclinic; a 13.818(5); b 14.196(5); c 14.295(5) Å; α 114.53(3); β 111.00(3); γ 98.32(3)°; space group $P1$, $Z = 2$.

The unit cell parameters and intensities of 4224 reflections were recorded with a SYNTEX P2$_1$ automatic diffractometer (Mo-K_α, graphite monochromator, $\theta/2\theta$-scan, 2θ 48°).

The structure was solved by the heavy-atom method and refined by full-matrix least squares, anisotropically (Ni, Cr(1), Cr(2), S(1), S(2), O(1), O(2) and all N atoms) and isotropically to $R = 0.076$, $R_w = 0.071$. Calculations were performed by the XTL-SYNTEX program package on a NOVA-1200 computer. Atomic coordinates are listed in Table 6.

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