chloromethane 5:95 v/v); ^{31}P NMR (162 MHz, CD_2Cl_2) δ −4.3; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.30 (1 H, br s, NH), 7.02 (1 H, q, H_6 of T), 6.18 (1 H, dd, $H_{1'}$), 4.68 (1 H, m, $H_{3'}$), 4.58 (1 H, m, $H_{5''}$), 4.35 (1 H, m, $H_{5'}$), 4.16 (2 H, m, H_a), 3.91 (1 H, m, $H_{4'}$), 2.61 (1 H, m, $H_{2''}$), 2.54 (1 H, m, $H_{2'}$), 1.93 (3 H, d, CH_3 of T), 1.75 (2 H, m, H_b), 1.47 (2 H, m, H_c), 0.98 (3 H, t, H_d); ^{13}C NMR (100.64 MHz, CD_2Cl_2) δ 164.3 (C_2 or C_4 of T), 150.5 (C_4 or C_2 of T), 136.6 (C_6 of T), 112.1 (C_5 of T), 86.4 ($C_{1'}$), 78.3 ($C_{3'}$, $^2J_{POC}$ = 5.5 Hz), 74.3 ($C_{4'}$, $^3J_{POCC}$ = 7.7 Hz), 69.8 ($C_{5'}$, $^2J_{POC}$ = 9.0 Hz), 68.4 (C_a, $^2J_{POC}$ = 5.9 Hz), 35.4 ($C_{2'}$, $^3J_{POCC}$ = 8.4 Hz), 32.5 (C_b, $^3J_{POCC}$ = 9.9 Hz), 19.1 (C_c), 13.7 (C_d), 12.5 (CH_3 of T).

Pentacoordinated Compounds 4, 5, and 13–15. In order to avoid decomposition during handling and purification, we prepared the P^V compounds **4**, **5**, and **13–15** in situ in NMR tubes. These syntheses were carried out by addition of 1 equiv of tetrachloro-1,2-benzoquinone to the corresponding phosphites, dissolved in CD_2Cl_2 at −80 °C. The NMR tubes were flushed with dry argon and sealed. After 1 h, the NMR samples were transferred into the NMR instrument, which had been stabilized at constant temperature (20 °C for **4**, **14**, and **15**; −41 °C for **5** and **13**), and the ^{1}H- and ^{31}P-NMR spectra were recorded. The identity of the P^V-TBP systems was established on the basis of ^{1}H- and ^{31}P-NMR spectroscopy, which showed >95% purity in each case.

Compound 4: ^{31}P NMR (81 MHz, CD_2Cl_2, 20 °C) δ −43.3; ^{1}H NMR (600 MHz, CD_2Cl_2, 20 °C) δ 9.00 (1 H, br s, NH), 7.05 (1 H, q, H_6 of T), 6.17 (1 H, dd, $H_{1'}$), 4.76 (1 H, m, $H_{3'}$), 4.73 (1 H, m, $H_{5''}$), 4.20 (1 H, m, $H_{5'}$), 3.98 (1 H, m, $H_{4'}$), 3.93 (3 H, d, OCH_3, $^3J_{POCH}$ = 14.3 Hz), 2.48 (1 H, m, $H_{2''}$), 2.44 (1 H, m, $H_{2'}$), 1.93 (3 H, d, CH_3 of T).

Compound 5: ^{31}P NMR (162 MHz, CD_2Cl_2, −41 °C) δ −44.7; ^{1}H NMR (400 MHz, CD_2Cl_2, −41 °C) δ 10.29 (1 H, br s, NH), 7.12 (1 H, q, H_6 of T), 6.31 (1 H, dd, $H_{1'}$), 4.82 (1 H, m, $H_{3'}$), 4.75 (1 H, m, $H_{5''}$), 4.53–4.32 (2 H, m, H_a), 4.23 (1 H, m, $H_{5'}$), 4.00 (1 H, m, $H_{4'}$), 3.74–3.55 (2 H, m, H_b), 3.38 (3 H, s, OCH_3), 2.53 (1 H, m, $H_{2''}$), 2.43 (1 H, m, $H_{2'}$), 1.96 (3 H, d, CH_3 of T).

Compound 13: ^{31}P NMR (162 MHz, CD_2Cl_2, −41 °C) δ −44.7; ^{1}H NMR (400 MHz, CD_2Cl_2, −41 °C) δ 10.84 (1 H, br s, NH), 7.12 (1 H, q, H_6 of T), 6.30 (1 H, dd, $H_{1'}$), 4.78 (1 H, m, $H_{3'}$), 4.74 (1 H, m, $H_{5''}$), 4.28 (2 H, m, H_a), 4.20 (1 H, m, $H_{5'}$), 4.03 (1 H, m, $H_{4'}$), 2.52 (1 H, m, $H_{2''}$), 2.44 (1 H, m, $H_{2'}$), 1.97 (3 H, d, CH_3 of T), 1.67 (2 H, m, H_b), 1.39 (2 H, m, H_c), 0.96 (3 H, t, H_d).

Compound 14: ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C) δ −46.3; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.58 (1 H, m, H_{5b}), 4.30 (3 H, m, H_1 and H_a), 3.96 (1 H, m, H_{5a}), 3.56 (2 H, m, H_b), 3.36 (3 H, s, OCH_3), 2.25–1.20 (7 H, m, H_6, H_{7a}, H_{7b}, H_{8a}, H_{8b}, H_{9a}, H_{9b}).[25b]

Compound 15: ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C) δ −22.6; ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C) δ 4.20 (2 H, m, H_a), 4.15 (4 H, m, Hs of the 5-ring), 3.52 (2 H, m, H_b), 3.30 (3 H, s, OCH_3).

Acknowledgment. The authors thank Mr. L. J. M. van de Ven for his help in the analysis of the ^{1}H NMR spectra.

Supplementary Material Available: Two-dimensional ^{31}P–^{1}H and ^{13}C–^{1}H correlation maps measured for the cyclic 3′,5′-phosphites and cyclic 3′,5′-phosphates **6–9** and a calculated graph of $J_{H_1H_3} + J_{H_1H_4} + J_{H_2H_3} + J_{H_2H_4}$ vs torsion angle $[H_1–C_a–C_b–H_3]$ (10 pages). Ordering information is given on any current masthead.

Multinuclear NMR Study of the Crystal Field Strength of the Nitro Ligand and the Empirical Estimation of the ^{59}Co NMR Chemical Shifts of Cobalt–Nitro Complexes

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Abstract: The variable ligand field strength of the nitro ligand has been reexamined on the basis of a steric model. An improved empirical method is proposed for the estimation of nitro ligand field strength in terms of a single correction parameter Δ_s (1.824×10^{-6} ppm^{-1}) to the shift parameter S_{NO_2} (3.075×10^{-5} ppm^{-1}) for the estimation of the ^{59}Co NMR chemical shifts of cobalt–nitro complexes. The reversed chemical shift trend of geometrical isomers of cobalt–nitro complexes are attributed to variations in the $10Dq$ of the nitro ligands. The model is applied to the assignment of different isomers of cobalt–nitro compounds obtained from ligand exchange reactions of the cobaltinitrite anion with the N_3^- and SCN^- ions. In all the ligand exchange reactions studied, it was found that mixed nitro complexes formed in the reaction predominately adopted the trans configuration.

Introduction

Some time ago, it was demonstrated[1] that the isotropic ^{59}Co NMR chemical shift for the entire range of orthoaxial six-coordinated diamagnetic cobalt(III) complexes relative to $[Co(CN)_6]^{3-}$, could be reasonably estimated by using the empirical equation

$$\delta(\text{ppm}) = \frac{1}{3}\left(\frac{1}{S_1 + S_2} + \frac{1}{S_3 + S_4} + \frac{1}{S_5 + S_6}\right) - 11000 \qquad (1)$$

where S_1 and S_2, S_3 and S_4, S_5 and S_6 are parameters characteristic of the ligands on the x, y, and z axis, respectively. This expression calculates the chemical shift of any cobalt complexes with a given set of S_L parameters[1] for all the different ligands encountered and was developed based on the well-established inverse relationship between the ^{59}Co chemical shifts and the energies of the first spin-allowed ($^1T_{1g}$) electronic transition of octahedral CoA_6 complexes.[2,3] The model successfully predicts the order of the chemical shifts for a large variety of low-symmetry geometrical isomers, i.e., cis is more shielded than trans, and similarly fac is more shielded than mer isomers, which have been demonstrated experimentally both by ^{59}Co NMR[4] as well as by optical data.[5] But the model fails to predict the correct chemical shifts and shielding trend when cobalt(III)–nitro complexes were encountered. In another article,[6] an empirical formula was

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proposed to account for the variation of the ligand field strength of the nitro ligand

$$S_{NO_2} = (3.096 - 0.093n_{cis} - 0.023n_{trans}) \times 10^{-5}\ \text{ppm}^{-1} \quad (2)$$

where n_{cis} is the number of NO_2^- ligands cis to the NO_2^- for which the shift parameter is required and n_{trans} is the corresponding number of trans ligands. Equation 2, which is the solution of a numerical analysis based on the observed chemical shifts for the series $[Co(NH_3)_{6-x}(NO_2)_x]^{3-x}$, suggests that the nitro ligand field strength varies depending on the number of nitro ligands bonded to the same complex and has been shown convincingly in a number of occasions by ^{59}Co NMR studies.[7-9]

The present paper is concerned with (i) the origin of this variation as well as the ligand field strength of the nitrite ion in the spectrochemical series and (ii) the spectroscopic properties of three series of mixed-ligand (monodentate) cobalt complexes containing more than one nitro group for which chemical shifts were predicted by eq 1 with an improved method for estimating the shift parameter (eq 2) to account for the steric effect of nitro ligand in cobalt(III) complexes. Examples are presented demonstrating that both normal and reverse shielding trends were observed for geometrical isomer pairs involving nitro ligands of diamagnetic cobalt(III) complexes belonging to the series $[Co(NO_2)_{6-x}(NCS)_x]^{3-x}$ and $[Co(NO_2)_{6-x}(SCN)_x]^{3-x}$.

Experimental Section

Cobalt(III)–nitro–amine complexes were synthesized following standard procedures. Reagent grade sodium cobaltinitrite was purchased from Strem Chemicals. U.S.A. and was used without further purification. All other reagents were BDH reagent grade.

The ligand exchange reactions between the $Co(NO_2)_6^{3-}$ anion and the ligand X (where X = N_3^-. NCS^-, and NH_2OH) were carried out in this work. A typical experiment involved the observation of the NMR spectra of a reaction mixture obtained by mixing ligand to cobaltinitrite anion at a molar ratio of 10 in D_2O (1 M X/0.1 M $Na_3Co(NO_2)_6$) at room temperature.

The ^{17}O, ^{14}N. ^{59}Co NMR spectra were recorded on a Bruker WM-250 (5.8749 T) superconducting Fourier Transform Pulse NMR spectrometer operating at 33.892, 18.059. and 59.035 MHz, respectively. The pulse length was 28, 81, and 28 μs for the regular 90° pulse correspondingly. The spectra were recorded in aqueous solution at the probe temperature of 295.3 K and was found to have a ±0.02 K drift. Samples were contained in 10 mm (o.d.) round-bottomed tubes purchased from Wilmad Glass Co. Chemical shifts were reported relative to external $[Co(CN)_6]^{3-}$ and were obtained by direct frequency measurements. Susceptibility corrections were neglected because they were small (1–2 ppm) compared to the ^{59}Co NMR chemical shift range. Line widths were measured at full width at half height of the absorption signal. Good solubility was obtained with all the compounds and systems studied, a typical spectrum required no more than 10000 pulses for ^{59}Co NMR and 100000 pulses for ^{14}N and ^{17}O NMR. Exponential multiplication of the FID was used where necessary for spectral processing.

Results

When cobaltinitrite and hydroxyamine was mixed, decomposition of the complex via oxidation of the ligands occurred rapidly and was too fast to be observed by NMR. The final solution displaced a pink color characteristic of cobalt(II) ions. No ^{59}Co NMR spectrum was observed.

Table I. Summary of ^{14}N NMR Data from the Reaction of $Na_3[Co(NO_2)_6]$ (0.1 M) with (i) NaN_3 (1 M) and (ii) NaSCN (1 M)

δ_{obs},[a] ppm	suggested assignment
	N_3^- Reaction
−127 (28)[b]	uncomplexed azide[c]—centered N
−274 (84)	uncompleed azide—terminal N
236 (171)	free nitro ligand
−121 (sh)	tentatively assigned to complexed nitro group
−239 (200)	$M-N_\alpha-N-N$
−333 (br 350)	$M-N-N_\beta-N$
−354 (br 350)	$M-N-N-N_\gamma$
	NCS^- Reaction
360 (br sh)	
315 (640)	
45 (br)[d]	complexed nitro group(?)
0.5 (10)	uncomplexed NCS^-
−70[d]	tentatively assigned to M–SCN
−215	
−240 (overlapping)	M–NCS
−265	

[a] Chemical shifts referenced to external CH_3NO_2. [b] Values in parnetheses are line widths in Hz. [c] The term uncomplexed as opposed to free ligand is used to make the distinction that ligands not complexed may be involved in other dynamic processes. [d] New signals observed from t_∞ (overnight) spectrum.

^{14}N NMR Spectra. The ^{14}N NMR data for the ligand exchange reactions of cobaltinitrite with N_3^- and NCS^- is summarized in Table I. In both cases, nitrogen complexation was observed, therefore firmly establishing first sphere ligand exchange. An electron-transfer mechanism has been proposed for the ligand exchange reaction of cobaltinitrite anion and has been discussed elsewhere.[6] The observed ^{14}N NMR chemical shifts were referenced to external nitromethane and were generally consistent with known literature values.[10] Uncomplexed azide was observed at −127 and −274 ppm for the centered and terminal nitrogen, respectively.[11] These shifts compared favorably with a 1 M sodium azide solution giving two signals at −129 and −276 ppm with corresponding line widths of 49 and 118 Hz. A trace amount of dissociated nitrite was also observed at 236 ppm compared with 227 ppm for a 1 M sodium nitrite solution in D_2O. The broad (weak) signal at 68 ppm is assigned to the complexed nitrite. The chemical shift for complexed nitrite may be compared with the value of 44–46 ppm for rhodium complexes[12] and 93 ppm for cobaltinitrite[13] after converting to the nitromethane reference. The group of signals from −121 to −354 ppm fell well within the known chemical shift range for complexed azide. The peaks at the higher fields likely correspond to the α nitrogen in $M-N_\alpha-N_\beta-N_\gamma$. These were observed to be broader as expected (see Table I). The large numbers of observed peaks in this region suggested that either more than one type of ligand is trans to the azide or geometrical isomers involving the azide may result in different ^{14}N chemical shifts. At present, it is not possible to make detailed assignments for this group of ^{14}N signals. Further work is in progress.

The ligand exchange reaction with the thiocyanate anion proceeded rapidly, and the ^{14}N NMR spectrum of the reaction mixture confirmed that both modes of complexation took place. The signal at −70 ppm was assigned to the sulfur bonded mode, and the nitrogen bonded complexes were assigned to the group of overlapping signals at −215 to −265 ppm. Complexed nitro was observed at 45 ppm, and uncomplexed NCS^- was observed at 0.5 ppm (the ^{14}N NMR signal for a 1 M NaSCN D_2O solution was observed at −170 ppm). This substantial low field shift of the NCS^- may be associated with the well-known effect of paramagnetic ions such as Co(II) generated in the electron-transfer reaction.[13] Two unexpected low field signals at 315 and 360 ppm accounting for as much as 50% of the total product signal intensities cannot be assigned without further work. A conjecture based on the position of their chemical shifts and considerations of their line widths suggests that nitrosyl complexes may be formed in the reaction. Well-established examples of nitrosyl complexes such as $[Tc(NO)(NCS)_5]^{2-}$ and $[Tc(NO)(NCS)_5]^{3-}$ have been prepared under similar conditions.[14] The present reaction conditions coupled with the favorable redox properties of cobaltinitrite may well provide the condition for their formation and perhaps

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Table II. Summary of ^{17}O NMR Data from the Reaction of $Na_3[Co(NO_2)_6]$ (0.1 M) with (i) NaN_3 (1 M) and (ii) NaSCN (1 M)

δ_{obs},[a] ppm	suggested assignment
	N_3^- Reaction
665 (trace amount)	uncomplexed nitro group
	NCS^- Reaction
10 (br)	complexed water in $[Co(NO_2)_5D_2O]^{2-}$
94 (1846)	complexed D_2O to Co^{2+}
417 (20)	NO_3^- ion

[a] Chemical shifts referenced to external H_2O.

Table III. ^{59}Co NMR Data from the Reaction of NaN_3 (1.0 M) and $Na_3[Co(NO_2)_6]$ (0.1 M) in D_2O

	δ_{cal},[a,b] ppm		
δ_{obs}, ppm	eq 2[c]	this work[d]	suggested assignment(s)
			NO_2^-–N_3^- (8)[e]
8369	8399	8376	t-$Co(NO_2)_4(N_3)_2^{3-}$
8937	8871	8940	f-$Co(NO_2)_3(N_3)_3^{3-}$
9009	9069	9001	m-$Co(NO_2)_3(N_3)_3^{3-}$
10133	10089	10123	t-$Co(NO_2)_2(N_3)_4^{3-}$
11113	11093	11119	$Co(NO_2)(N_3)_5^{3-}$
12558	12558	12558	$Co(N_3)_6^{3-}$
			NO_2^-–N_3^-–ONO^- (22)
8804	8787	8801	t,t-$Co(NO_2)_3(N_3)_2(ONO)^{3-}$
9268	9194	9241	c,c,c-$Co(NO_2)_2(N_3)_2(ONO)_2^{3-}$
9300	9343	9339	t,c,c-$Co(NO_2)_2(N_3)_2(ONO)_2^{3-}$
9529	9467	9516	c,c-$Co(NO_2)_2(N_3)_3(ONO)^{3-}$
10848	10830	10854	t-$Co(NO_2)(N_3)_4(ONO)^{3-}$
			NO_2^-–N_3^-–H_2O (22)
8553	8558	8592	c-$Co(NO_2)_4(H_2O)(N_3)^-$
9477	9426	9499	c,c-$Co(NO_2)_3(H_2O)_2(N_3)^-$
9780	9740	9758	t,c-$Co(NO_2)_3(H_2O)_2(N_3)^-$
	9704	9779	f-$Co(NO_2)_3(H_2O)_3$
9960	9897	9913	t.t-$Co(NO_2)_3(H_2O)_2(N_3)^-$
10507	10522	10519	t,t-$Co(NO_2)_2(H_2O)(N_3)_3^{2-}$
10978	10957	10953	t.t,t-$Co(NO_2)_2(H_2O)_2(N_3)_2^-$
			NO_2^-–N_3^-–ONO^-–H_2O (40)
10469	10483	10479	t,c-$Co(NO_2)_2(H_2O)(N_3)(ONO)^-$
10550	10564	10560	t,t-$Co(NO_2)_2(H_2O)_2(N_3)(ONO)^-$
10814	10791	10815	t,c-$Co(NO_2)(H_2O)(N_3)_2(ONO)_2^{2-}$
11156	11172	11198	t,t.t-$Co(NO_2)(N_3)(ONO)_2(H_2O)_2^-$
			Others
9844	9816	9865	c,c,c-$Co(NO_2)_2(H_2O)_2(ONO)_2^-$
	9821	9869	c.c.t-$Co(NO_2)_2(N_3)_2(H_2O)(ONO)^{2-}$

[a] $S_{N_3^-} = 2.1224 \times 10^{-5}$ ppm^{-1}, $S_{ONO^-} = 2.3462 \times 10^{-5}$ ppm^{-1}. $S_{H_2O} = 1.920 \times 10^{-5}$ ppm^{-1}. [b] Standard deviation is calculated based on the differences between observed chemical shifts and calculated chemical shifts ($\delta_{obs} - \delta_{cal}$). When more than one assignment is suggested, the data are not included in the calculation of the standard deviation. [c] Standard deviation = 38 ppm. [d] Standard deviation = 22 ppm. [e] Values in parentheses indicate the number of expected isomers other than the parent species.

a potential preparative route to cobalt nitrosyl complexes.

^{17}O NMR Spectra. The ^{17}O NMR data for the two reactions is given in Table II. In both cases, only trace quantities of the uncomplexed nitrite (665 ppm) and/or nitrate (417 ppm) were observed in both reactions. The chemical shifts of a 1 M sodium nitrite and a 1 M sodium nitrate solution were detected at 663 and 416 ppm, respectively. A large low field shift was also observed for the water resonance at 94 ppm. This water peak has a line width of 1846 Hz. This observation was consistent with the results obtained from ^{14}N NMR whereby a substantial low field shift was also observed for the NCS^- ion. The signal at 10 ppm accounting for about 20% of the total line intensities in the ^{17}O spectrum is tentatively assigned to the pentanitro–aquo–cobalt complex by comparison with previous studies[6] of the ligand exchange reaction of cobaltinitrite with amine ligands.

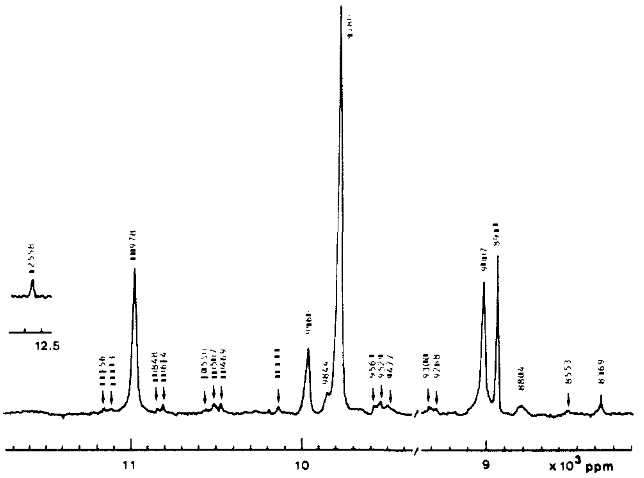

Figure 1. 59.035-MHz (5.8719 T) ^{59}Co NMR spectrum of 0.1 M sodium cobaltinitrite and 1.0 M sodium azide immediately after mixing.

Table IV. ^{59}Co NMR Data from the Reaction of NaSCN (1.0 M) and $Na_3[Co(NO_2)_6]$ (0.1 M) in D_2O

	δ_{cal},[a,b] ppm		
δ_{obs}, ppm	eq 2[c]	this work	suggested assignment(s)
			NO_2^-–NCS^- (8)[e]
7448 (67)[b]	7511	7449	$Co(NO_2)_6^{3-}$
7269 (147)	7277	7255	t-$Co(NO_2)_4(NCS)_2^{3-}$
7668 (184)	7566	7629	f-$Co(NO_2)_3(NCS)_3^{3-}$
7858 (172)	7886	7882	t-$Co(NO_2)_2(NCS)_4^{3-}$
8445	8444	8467	$Co(NO_2)(NCS)_5^{3-}$
			NO_2^-–SCN^- (8)
7790 (190)	7755	7784	c-$Co(NO_2)_4(SCN)_2^{3-}$
7738 (166)	7736	7713	t-$Co(NO_2)_4(SCN)_2^{3-}$
8202 (211)	8127	8191	f-$Co(NO_2)_3(SCN)_3^{3-}$
8188	8158	8172	m-$Co(NO_2)_3(SCN)_3^{3-}$
8739 (220)	8718	8763	c-$Co(NO_2)_2(SCN)_4^{3-}$
10568 (10)	10568	10568	$Co(SCN)_6^{3-}$
			NO_2^-–NCS^-–SCN^- (24)
8287	8260	8305	c,t,c-$Co(NO_2)_2(NCS)_2(SCN)_2^{3-}$
8919	8903	8925	t,t-$Co(NCS)_3(SCN)_2(NO_2)^{3-}$
			Other(s)
8042	8411	8036	t-$Co(NO_2)_4(SCN)(H_2O)^{2-}$
8257	8258	8255	t,t,t-$Co(NO_2)_2(NCS)_2(ONO)_2^{3-}$
	8248	8245	t.c,c-$Co(NO_2)_2(NCS)_2(ONO)_2^{3-}$
10651	10614	10642	t,c-$Co(ONO)_2(H_2O)_2(NO_2)(SCN)^-$
	10648	10648	t,t-$Co(ONO)_3(NCS)_2(H_2O)^{2-}$
10675	10648	10676	c,t,c-$Co(H_2O)_2(SCN)_2(NO_2)(ONO)^-$
	10687	10683	t.t-$Co(H_2O)_3(NO_2)_2(NCS)$

[a] S_L values obtained from ref 1; $S_{NCS^-} = 2.4761 \times 10^{-5}$ ppm^{-1}, $S_{SCN^-} = 2.3182 \times 10^{-5}$ ppm^{-1}, $S_{ONO^-} = 2.3462 \times 10^{-5}$ ppm^{-1}, $S_{H_2O} = 1.9200 \times 10^{-5}$ ppm^{-1}. [b] See footnote *b* Table III. [c] Standard deviation = 108 ppm. [d] Standard deviation = 18 ppm. [e] See footnote *e* of Table III.

^{59}Co NMR Spectra. The ^{59}Co NMR spectra for the ligand exchange reaction between cobaltinitrite and sodium azide is given in Figure 1. Immediately after mixing, the ^{59}Co NMR spectra exhibited complex features. Eight strong peaks and groups of weak signals over the chemical shift range of 4000 ppm were observed in the NMR spectrum. The ^{59}Co NMR spectrum for the reaction mixture containing 0.1 M sodium cobaltinitrite and 1 M potassium thiocyanate immediately after mixing is given in Figure 2. A total of 18 signals were observed immediately after mixing. With one or two exceptions, all observed signals were sharp with narrow line widths generally below 200 Hz and typically between 150 and 180 Hz. The chemical shifts in the two spectra are summarized in Tables III and IV. Spectral assignments were carried out with the help of eq 1 discussed in the following section.

^{15}N and ^{33}S NMR. Repeated attempts to observe the ^{15}N as well as the ^{33}S NMR spectra were unsuccessful.

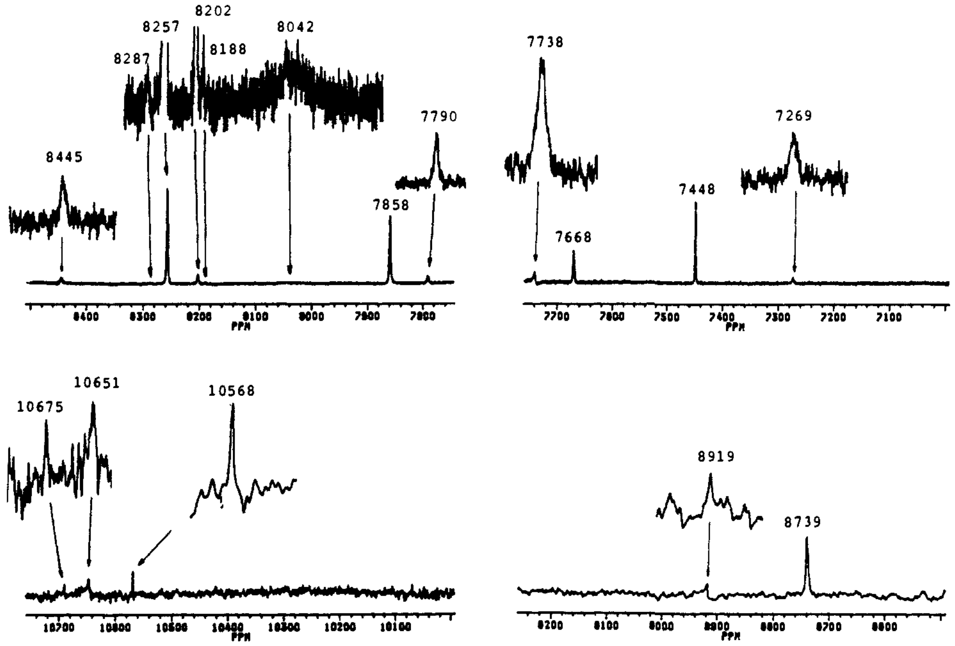

Figure 2. 59.035-MHz (5.8719 T) ^{59}Co NMR spectrum of 0.1 M sodium cobaltinitrite and 1.0 M potassium thiocyanate immediately after mixing.

Discussion

The theory of the effect of geometrical isomerism on metal chemical shifts has been treated by Juranić.[15] A comprehensive review on the ligand field interpretation of metal chemical shifts in octahedral d^6 transition-metal complexes, also by Juranić, has appeared recently.[16] The reader is referred to these two articles for a theoretical treatment of the subject.

A. ^{59}Co NMR Chemical Shift of Cobalt-Nitro Complexes. Several papers[6,7] have attempted to rationalize the observed ^{59}Co NMR shifts of Co(III) complexes containing nitro ligands. The chemical shifts for the $[Co(NO_2)_{6-x}(NH_3)_x]^{3-x}$ series calculated by using 1 (with a constant shift parameter, S_L, for NO_2^-) resulted in large deviations from observed values. The deviations are not likely due to large changes in the orbital reduction factors because the variation in the orbital reduction factors for NH_3 and NO_2^- ligands is relatively small.[7] Since the ligator atoms belong to the same period, small variation of the nephelauxetic ratio, β_{35}, is also anticipated from complex to complex in the same series.[17] It was suggested that the steric repulsion interactions between NO_2^- ligands is mainly responsible for the deviations in the calculated and observed chemical shifts because the negative charge on the nitro group is localized on the oxygen atoms,[18] consequently leading to changes in $10Dq$. This model is consistent with earlier optical spectroscopy studies of coordination compounds which led to the suggestion that steric crowding in a complex may influence the manner of coordination adopted by ligands including nitrite.[19-23]

Table V. Summary of Effective $S_{NO_2}{}^a$ for $[Co(NO_2)_{6-x}L_x]^{3-x}$ Complexes (L = Monodentate Ligands)

X	isomer	effective S_{NO_2} (10^{-5} ppm^{-1})
0	x = y = z	$3.075 - 2\Delta_s$
1	x = y	$3.075 - 3\Delta_s/2$
	z	$3.075 - 2\Delta_s$
2	x = y } (cis)	$3.075 - 3\Delta_s/2$
	z } (cis)	$3.075 - \Delta_s$
	x = y (trans)	$3.075 - \Delta_s$
3	x = y = z (fac)	$3.075 - \Delta_s$
	x } (mer)	$3.075 - \Delta_s$
	z } (mer)	$3.075 - \Delta_s/2$
4	x = y (cis)	$3.075 - \Delta_s/2$
	z (trans)	3.075
5	z	3.075

$^a\Delta_s = 0.1824 \times 10^{-5}$ ppm^{-1}.

The numerical expression 2 was derived from the observed chemical shifts of the $[Co(NH_3)_{6-x}(NO_2)_x]^{3-x}$ series which is the only known "complete" mixed-ligand (monodentate) series involving nitro groups complexed to cobalt. Chemical shifts calculated by using eq 1 and 2 were applied in the assignment of observed ^{59}Co NMR resonances for reaction mixtures of ethylenediamine and cobaltinitrite as well as cyanide and cobaltinitrite.[6] If the origin of the aforementioned deviations of the observed chemical shifts from calculated shifts were characteristic of sterically interacting *neighboring* nitro ligands, the interactions between the nitro groups that are cis to each other is expected to be dominant and its separation into the cis and the trans effect would be difficult as suggested by eq 2. A more reasonable approach is to assume that the nitro ligands exert "almost equal" steric effects toward each other by the correction Δ_s (subscript s symbolizes steric effect and is defined as the steric effect per pair of nitro ligands cis to each other), so the shift parameter S_{NO_2} for each nitro ligand in the complex can be easily calculated by counting the number of nitro neighbors. For example, for the cobalt(III) complex with the general formula c-$Co(NO_2)_4B_2$, the interaction of each axial nitro ligand with the two equatorial nitro groups results in a total ligand field correction of Δ_s because the correction from each nitro group contributes $\Delta_s/2$, whereas the correction to the ligand field strength of the equatorial nitro is $3\Delta_s/2$ since the interaction of the two equatorial nitro groups must be taken into consideration. Table V summarizes the correct S_{NO_2} for the $CoA_{6-x}(NO_2)_x$ series. The numerical value for Δ_s was obtained by best fitting the ^{59}Co NMR chemical shifts data for the $[Co(NH_3)_{6-x}(NO_2)_x]^{3-x}$ series (Table VI) into eq 1 using the corrected S_{NO_2} expressions in Table V. The best fitted values are $S_{NO_2} = 3.075 \times 10^{-5}$ ppm^{-1} and $\Delta_s = 1.824 \times 10^{-6}$ ppm^{-1} assuming the ligand field strength of NH_3 is approximately constant. The average deviation of the calculated chemical shifts for this series using the above values is ±25 ppm. In contrast to the value given in expression 2, the lower S_{NO_2} value obtained by using this procedure placed the ligand field strength of the nitro group closer to the ligand field strength of hydroxyammine in the

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Table VI. ^{59}Co NMR Chemical Shift Data for $[Co(NO_2)_{6-x}(NH_3)_x]^{3-x}$

complexes	chemical shifts, ppm δ_{obs}	eq 2^{a,b}	this work^c
$Co(NO_2)_6^{3-}$	7448 (56)^d	7511	7449
$Co(NO_2)_5(NH_3)^{2-}$	7182	7182	7167
c-$Co(NO_2)_4(NH_3)_2^-$		7061	7087
t-$Co(NO_2)_4(NH_3)_2^-$	6905 (1750)^e	6935	6915
m-$Co(NO_2)_3(NH_3)_3$	6981 (782)	7024	7038
f-$Co(NO_2)_3(NH_3)_3$	7205 (150)	7122	7181
c-$Co(NO_2)_2(NH_3)_4^+$	7277 (331)	7272	7315
t-$Co(NO_2)_2(NH_3)_4^+$	7207 (355)	7204	7203
$Co(NO_2)(NH_3)_5^{2+}$	7629 (185)	7625	7649
$Co(NH_3)_6^{3+}$	8175 (172)	8175	8175

^{a}See footnote *b* of Table III. ^{b}Standard deviation = 41 ppm. ^{c}Standard deviation = 25 ppm. ^{d}Values in parentehses are line widths in Hz. ^{e}Reference 4.

Table VII. Single Crystal ^{59}Co NMR Data^a

complex	percent σ_{xx}	σ_{yy}	σ_{zz}	calculated^b K_1	K_2
t-$[Coen_2Cl_2]Cl\cdot HCl\cdot 2H_2O$	-10.6	-10.9	-6.1	4.23	3.90
t-$[Coen_2(NO_2)_2]NO_3$	-6.2	-6.5	-6.1	4.01	4.36

^{a}Data obtained from ref 25. ^{b}Calculation using $\Delta E(^1A_{2g} - {}^1A_{1g})$ = 23 000 and $\Delta E(^1E_g - {}^1A_{1g})$ = 16 600 cm^{-1} for the dichloro complex.[41] The transition energies for the dinitro complex are 22 000 and 23 000 cm^{-1}, respectively.[16]

spectrochemical series for a monosubstituted cobalt(III) complex which has been suggested by earlier optical spectroscopy study of nitro–amine–cobalt compounds.[24]

A check on the validity of the steric model is provided by the single-crystal measurement study of the chemical shift anisotropy of t-$[Coen_2X_2]^+$ (X = NO_2^- and Cl^-) by Hartmann and coworkers.[25] Their results for the two compounds are summarized in Table VII. From the anisotropies listed in Table VII, the $(1/r^3)_c(k')^2$ values can be calculated using 3[26]

$$\sigma^p = -9.29 \times 10^3 \langle r^{-3}\rangle_c (k')^2 \Delta E^{-1} \quad (3)$$

where the symbols have their usual meaning, i.e., $\langle r^{-3}\rangle_c$ are the appropriate radial factors and the $(k')^2$ is the orbital reduction factor. Fujiwara and co-workers[26] have pointed out that the orbital reduction term and the radial term are best treated together $\langle r^{-3}\rangle_c (k')^2 = K$ for the extraction of M–L covalency information since independent evaluation of the two factors, although possible, is unreliable. There have been some attempts recently to calculate these parameters by empirical methods.[27] The calculated K_i values are listed in the last two columns of the same table. The differences in K_1 and K_2 (see eqs 4 and 5) for both complexes are small and are well within the prediction of the ^{59}Co NMR theory lending support to the commonly valid assumption stated earlier for nitro–amine complexes.

The mean values of the paramagnetic shielding for low-symmetry D_{4h} and C_{2v} cobalt complexes can be calculated when $K_1 = K_2 = K_3 = K_4 = 4.18$ au is substituted into eq 4 and 5[26,28]

$$\sigma^p(D_{4h}) = -9.29 \times 10^3[(1/3)K_1\Delta E^{-1}(^1A_{1g}-A_{2g}) + (2/3)K_2\Delta E^{-1}(^1A_{1g}-{}^1E_g)] \quad (4)$$

$$\sigma^p(C_{2v}) = -9.29 \times 10^3[(1/3)K_3\Delta E^{-1}(^1A_1-{}^1B_1) + (2/3)K_4\Delta E^{-1}(^1A_1-{}^1A_2,{}^1B_2)] \quad (5)$$

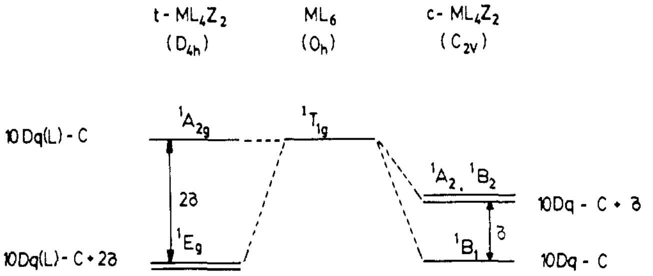

Figure 3. Correlation diagram for ML_6 and *cis,trans*-ML_4Z_2.

Assuming that compounds possessing C_{2v} symmetry is considered to have pseudotetragonal crystal field as suggested by Lever,[24] the appropriate crystal field splitting energies of the first excited $^1T_{1g}$ states of the ML_4Z_2 isomers can be related to their parent O_h compound by using the results of Lever[24] and Yamatera[29] (Figure 3), which relates the ΔE to the $10Dq$ of the L and the Z ligands. This method gave a calculated $\Delta\delta$ of +40 ppm ($\Delta\delta = \delta_{trans} - \delta_{cis}$) between the cis and trans isomer of $[Coen_2(NO_2)_2]^+$ which is opposite to the experimentally observed value $\Delta\delta$ of −228 ppm. If steric effect is the origin of this chemical shift trend reversal, the experimentally observed trend is anticipated when the appropriate prescribed ratio given in Table V is substituted for the correction of the $10Dq(NO_2^-)$ in ΔE^{-1} for the cis isomer. This procedure gives a calculated value of $\Delta\delta$ = −151 ppm in reasonable agreement with the experimental value. The choice of using the complex t-$[Coen_2(NO_2)_2]^+$ for illustration is determined by the limited availability of solid-state data in the literature. Despite the lack of solid-state data, the discussion presented here tends to support the idea that steric crowding between nitro groups is the most likely cause responsible for the observed chemical shift trend reversal for the cis and the trans isomer of cobalt–nitro complexes hence changes in $10Dq$. In making structural assignments involving ligands which are suspected of ligand mutual interactions, it is necessary to consider these possibilities particularly when line width measurements cannot provide meaningful differentiation.

B. The Assignment of ^{59}Co NMR Spectra of Cobalt(III) Complexes. The application to structural assignment using the proposed procedure will be illustrated with the ligand exchange reaction between (i) sodium cobaltinitrite and sodium azide and (ii) sodium cobaltinitrite and potassium thiocyanate. To our knowledge their ^{59}Co NMR spectra have not been reported previously.

Reactions of Cobaltinitrite Ion with Sodium Azide. In agreement with previous report,[6] the chemical shift of the most intense line in the spectrum of a freshly prepared solution mixture is at 7470 ± 5 ppm which is the cobaltinitrite anion. This line has a width of 55 Hz, corresponding to a T_2 of 5.6 ms. The assignment of all the lines in Figure 1 to members of the $[Co(NO_2)_{6-x}(N_3)_x]^{3-x}$ seems reasonable under the condition in which the concentration of the azide ion is 10-fold in excess. However, the calculated chemical shifts suggested that only the first three and the last readily discernible signals belong to members of this series. The signals at 8353, 8935, 9007, and 12 558 ppm were assigned to the t-$[Co(NO_2)_4(N_3)_2]^{3-}$ (calculated 8376 ppm), the f-$[Co(NO_2)_3(N_3)_3]^{3-}$ (calculated 8940 ppm), and the m-$[Co(NO_2)_3(N_3)_3]^{3-}$ (calculated 9002 ppm) isomers and the $[Co(N_3)_6]^{3-}$ anion, respectively. Additional support for the assignment of the fac and mer isomers comes from their observed line widths. The line widths for the fac and mer isomers are 290 and 877 Hz, respectively. The agreement is poor between the experimental line width ratio of 3 and the calculated line width ratio (based on a point charge model[30,31]) for the two isomers.

For ^{59}Co $I = 7/2$, in addition to the predominant quadrupolar relaxation, it has been shown that scalar relaxation of the second

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kind[32,33] as well as chemical shift anisotropy relaxation[34-36] also contributes to both T_1 and T_2 for cobalt complexes. The error associated with the estimation of the rotational correlation time τ_c is large for quadrupolar relaxation particularly in good hydrogen bonding solvents.[34,35] It is for this reason that line width correlation often has limited value in the identification of geometrical isomers in general. It is interesting to note that both the chemical shift trend (fac isomer is more shielded than mer isomers) and the line width trend (mer isomer is broader than fac isomer) observed in this example are consistent with the normal prediction.

The signal at 12 558 ppm was assigned to the symmetrical $[Co(N_3)_6]^{3-}$ with reasonable confidence based on both the calculated chemical shifts of 12 558 ppm and the line width. The assignment of the other peaks in the spectra were less straightforward. The strong and weak signals at 9780 ppm (line width 730 Hz) and 9960 ppm (line width 974 Hz) cannot be assigned to the cis and trans isomers of $[Co(N_3)_4(NO_2)_2]^{3-}$ ions, respectively (calculated chemical shifts 9909 and 10 126 ppm). Although it could be argued that the weaker of the two signals at 9960 ppm could be assigned to the cis isomer of this pair, they could also belong to the t,c- and t,t-$[Co(NO_2)_3(H_2O)_2(N_3)]^{3-}$ isomers (calculated 9758 and 9913 ppm, respectively) which were selected from the final short list of probable assignments. The criteria for a short list of probable assignments was ±50 ppm of the observed chemical shift value. This criteria was more reasonable compared to the lower value of ±25 ppm obtained in the fitting of the chemical shifts for the mix nitro–amine series $[Co(NO_2)_{6-x}(NH_3)_x]^{3-x}$ in order to make allowance for other factors which may affect the position of the ^{59}Co NMR chemical shifts. For example, solvent effects has been reported to be as much as 50 ppm for cobalt complexes.[37] Of the two remaining strong signals at 9844 and 10 978 ppm, the large separation in their chemical shifts warrants that they do not belong to any simple isomer pairs; the most reasonable assignments are the c,c,c-$[Co(NO_2)_2(ONO)_2(H_2O)_2]^-$ ion (calculated 9865 ppm) and the t,t,t-$[Co(NO_2)_2(N_3)_2(H_2O)_2]^-$ ion (calculated 10 953 ppm), respectively.

In the assignment of the weak signals, the peaks at 10 133 and 11 113 ppm were best ascribed to the missing members belonging to the NO_2^-–N_3^- series. They are the t-$[Co(N_3)_4(NO_2)_2]^{3-}$ (calculated 10 126 ppm) and the $[Co(N_3)_5(NO_2)]^{3-}$ (calculated 11 119 ppm) ions. The observed chemical shifts, the calculated shifts, and their suggested assignments are summarized in Table III. In Table III, the corresponding chemical shifts calculated by using eq 2 are also presented for comparison and no elaboration is required. Of the total 178 geometrical isomers possible for the different ligating configurations in the reaction of sodium azide with cobaltinitrite in aqueous solution, 22 signals were assigned with reasonable confidence. The standard deviation of the calculated from the experimental shifts was 22 ppm for the data in Table III.

Reactions with Sodium Thiocyanate. The thiocyanate ion is an ambidentate ligand with a nitrogen ligator atom on one end of the molecule and a sulfur ligator atom terminating the other end of the molecule. This arrangement provides a unique opportunity to study the differences in the ligand field strength between sulfur ligator and nitrogen ligator within one reaction system. If the deviations between the observed chemical shifts and the calculated chemical shifts as in eq 1 arise from effects other than that of a steric origin, a poor chemical shift correlation is expected since sulfur and nitrogen belong to a different period, therefore providing an excellent test for the present model.

Similar to the azide system, line width correlation is of little value in the structural identification of the observed species. Interpretation of the ^{14}N NMR result was complicated by the uncertainty of the possible formation of nitrosyl compounds discussed earlier. There are potentially 22 ligating configurations producing a total of 356 possible geometrical isomers for this system because of its ambidentate nature. Despite these complexities, most of the observed signals were readily assigned to the three ligating series containing NO_2^-–NCS^-, NO_2^-–SCN^-, and NO_2^-–NCS^-–SCN^-.

Four members of the $[Co(NO_2)_{6-x}(NCS)_x]^{3-x}$ series namely, $[Co(NO_2)_5(NCS)]^{3-}$, m-$[Co(NO_2)_3(NCS)_3]^{3-}$ and c-$[Co(NO_2)_2(NCS)_4]^{3-}$, were not observed in the NMR spectrum. The assignments of the other members of this series are the t-$[Co(NO_2)_4(NCS)_2]^{3-}$, f-$[Co(NO_2)_3(NCS)_3]^{3-}$, t-$[Co(NO_2)_2(NCS)_4]^{3-}$, and $[Co(NO_2)(NCS)_5]^{3-}$ ions at 7269, 7668, 7858, 8445 ppm, respectively. The signal at 7448 ppm was unambiguously assigned to the hexanitritecobaltic ion as discussed before. Table IV summarizes the ^{59}Co NMR chemical shifts data.

The signals at 7790, 7738, 8202, 8188, 8739, and 10 568 ppm were assigned to members belonging to the $[Co(NO_2)_{6-x}(SCN)_x]^{3-x}$ series. The lines at 7790 and 7738 ppm were assigned to the cis and trans isomer pair of the $[Co(NO_2)_4(SCN)_2]^{3-}$ ion (calculated 7784 and 7713 ppm), respectively. The signals at 8202 and 8188 ppm were assigned to the fac and mer isomer pair of the $\{Co(NO_2)_3(SCN)_3]^{3-}$ ion with calculated chemical shifts of 8191 and 8172 ppm, respectively. We note that calculation using eq 2 would have predicted (incorrectly) the normal fac and mer chemical shift trend for this isomer pair with calculated chemical shifts of 8127 and 8158 ppm, respectively. Only the cis isomer of the ion $[Co(NO_2)_2(SCN)_4]^{3-}$ was observed and was assigned to the signal at 8739 ppm (calculated 8763 ppm). The simple symmetrical ion $[Co(SCN)_6]^{3-}$, which has yet to be isolated, is assigned to the signal at 10 568 ppm (calculated 10 568 ppm) with confidence based on the considerations of both chemical shifts and observed line width (10 Hz). Of the expected 10 members of this series, only three members were not observed, namely, the $[Co(NO_2)_5(SCN)]^{3-}$, the t-$[Co(NO_2)_2(SCN)_4]^{3-}$, and the $[Co(NO_2)(SCN)_5]^{3-}$ ions. In contrast to the $[Co(NO_2)_{6-x}(N_3)_x]^{3-x}$ series, the cis–trans, fac–mer isomers were found to have reverse chemical shift trend for the two complex series $[Co(NO_2)_{6-x}(NCS)_x]^{3-}$ and $[Co(NO_2)_{6-x}(SCN)_x]^{3-}$.

Two members from the ligating configuration NO_2^-–NCS^-–SCN^- were observed. The signals at 8287 and 8919 were assigned to the complex c,t,c-$[Co(NO_2)_2(NCS)_2(SCN)_2]^{3-}$ (calculated 8305 ppm) and t,t-$[Co(NO_2)(NCS)_3(SCN)_2]^{3-}$ (calculated 8925 ppm). Of the remaining signals, the t-$[Co(NO_2)_4(SCN)(H_2O)]^{2-}$ ion was tentatively assigned to the signal at 8042 ppm (calculated 8036), and the signals at 8257, 10 651, and 10 675 ppm could not be assigned with certainty. In particular, the strong signal at 8257 ppm may well be responsible for the low field ^{14}N NMR signal at 315 and 360 ppm based on the consideration of peak area.

Conclusion

An improved empirical method is presented for the estimation of the variation of the ligand field strength of the nitro ligand which is dependent on the number of interacting nitro groups on the complex. In contrast to the two-parameter corrections proposed earlier (eq 2), the present model introduces a single correction parameter, Δ_s, to the S_L value of NO_2^- which has been demonstrated to produce the correct ligand field strength for nitro ligands in cobalt complexes. The ligand field strength of the nitro ligand in the monosubstituted nitrite complex is placed as a strong field ligand between cyanide and ethylenediamine in the spectrochemical series. For the systems studied in this paper, it was observed that most of the cobalt–nitro complexes took on a trans nitro geometry consistent with the proposed steric model whereby repelling nitro groups tend to arrange in a trans configuration to minimize electronic repulsion.

In agreement with earlier findings,[6] natural abundant ^{14}N and ^{17}O NMR confirmed the presence of free nitrate and is consistent with the electron-transfer mechanism[38,39] for ligand exchange

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proposed earlier whereby cobaltinitrite was reduced to Co^{2+}, and the nitrite was oxidized to free nitrate when the samples were left standing. In light of the complexity of the results obtained from the ligand exchange reaction involving the thiocyanate anion, care must be exercised in its interpreation, and further work is warranted to clarify the chemistry.

Finally, Juranič[40] reported that ^{59}Co NMR chemical shifts were sensitive to the ring size of chelating ligands, and we found evidence that ^{59}Co NMR chemical shifts were also highly sensitive to the stereochemical arrangement of chelating ligands during the course of this work. These findings will be reported in a future publication.

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Oxirenes and Ketocarbenes from α-Diazoketone Photolysis: Experiments in Rare Gas Matrices. Relative Stabilities and Isomerization Barriers from MNDOC-BWEN Calculations

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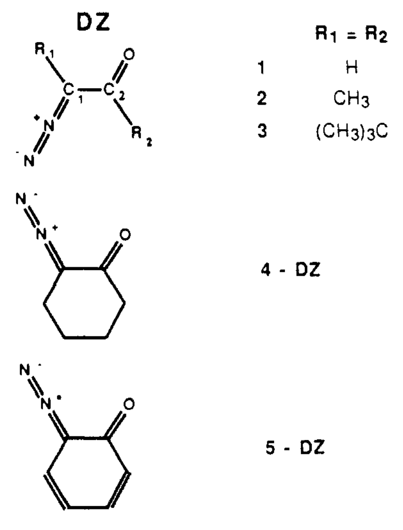
Contribution from Département de Chimie, Université Nationale de Côte d'Ivoire, 22 BP 582, Abidjan 22, Côte d'Ivoire, and Laboratoire de Physique des Interactions Ioniques et Moléculaires, URA CNRS 773, Université de Provence, Centre de Saint-Jérôme, Case 542, 13397 Marseille Cedex 13, France. *Received March 6, 1990. Revised Manuscript Received May 22, 1990*

Abstract: Matrix-isolated α-diazoketones (DZ) $RCOCN_2R$ ($R = CH_3$ or CD_3) were photolyzed and their reactions were monitored by FT-IR spectroscopy. The ketene (KE) products from the Wolff rearrangement were always more abundant than the α,β-unsaturated ketones (ON); this selectivity increased when a broad band source ($\lambda > 230$ nm) was used instead of a monochromatic laser source (457.9 nm). Oxirenes (OX) were detected as minor, but well-identified reaction products, stable at temperatures less than 25 K, even under the monochromatic irradiation; they isomerized to KE when irradiated at $\lambda > 230$ nm. With matrices doped with carbon monoxide, the reaction diverted toward ketoketene, which certainly resulted from ketocarbene (KC) trapped by CO molecules. The kinetic data showed that the rate constants of DZ → KC, KC → KE, KC → ON, and KC → OX processes have the same order of magnitude. After complete DZ photolysis, the KE concentration still increased under extended irradiation; therefore, $KC(T_0)$ is suspected to be another reaction product that slowly photoisomerized to KE. Some IR absorption bands might correspond to that intermediate, but unambiguous assignments could not be made. On the other hand, our previous oxirene identification has been supported by ab initio calculations at the SCF level, which justified the high-frequency value of oxirene $\nu(C{=}C)$. To account for the results of matrix isolation experiments and for those previously recorded during the gas-phase photolysis of several DZ [$R = CH_3$, $(CH_3)_3C$; $R\text{-}R = -(CH_2)_4-$], the relative stabilities of different isomers (KC, OX, and KE) were computed, and the assumed reaction paths from KC to reaction products were studied, in each series, through the MNDOC semiempirical method. Substituent effects and ring strain deeply influence the oxirene stability. Considering that the photolysis and photoisomerization processes occur on the singlet potential energy surface, we finally established a unified energy diagram, approximately scaled, that gathers together the different species in different electronic states and allows the interpretation of the main reaction features.

Since the initial publications,[3] a number of studies have dealt with the Wolff rearrangement (WR). Usually, the initial step consists of a photoinduced decomposition of an α-diazoketone (Scheme I). The ketocarbenes (KC), mainly obtained in photochemical conditions, are now currently observed and identified in ESR experiments (triplet state)[4-9] and through IR and UV-visible spectroscopies.[9] These studies, and our own results about the gas-phase photolysis of α-diazoketones,[10] have ruled out the hypothesis of a concerted mechanism proposed by Kaplan et al.[11,12]

Chart I



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