Ligand Substitution at Five-co-ordinate Centres: Associate Mechanism for the High-spin Complex 2,9-Dimethyl-1,10-phenanthrolinebis-(*OO*′-dimethyl dithiophosphato)nickel(II)

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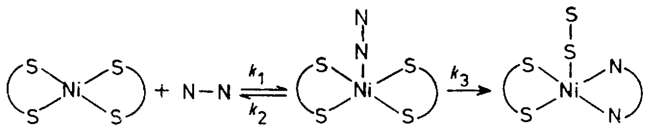
Summary The reaction between bis(*OO*′-dimethyl dithiophosphato)nickel(II) and 2,9-dimethyl-1,10-phenanthroline giving a high-spin five-co-ordinate adduct has been investigated; the adduct reacts with 2,2′-bipyridyl and 1,10-phenanthroline by an almost exclusively associative mechanism.

A NUMBER of kinetic studies involving reactions of low-spin five-co-ordinate 18-electron nickel(II) complexes have been reported recently.[1] In all cases the reactions followed a dissociative type mechanism in accordance with predictions based on Tolman's rules.[2] These rules do not apply to high-spin species. Therefore, high-spin five-co-ordinate nickel(II) complexes could react by either an associative or dissociative process. The associative mechanism leads to a 20-electron six-co-ordinate intermediate involving no spin change.

The *X*-ray structure of 2,9-dimethyl-1,10-phenanthrolinebis(*OO'*-dimethyl dithiophosphato)nickel(II), $[Ni\{S_2P(OMe)_2\}_2(dmphen)]$, shows that the complex is five-co-ordinate, one of the dithiophosphato ligands being monodentate while the other is bidentate. The magnetic moment of this complex is reported to be 3·2 BM.[3] We now report the kinetics and mechanisms of the substitution reactions of this complex with 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy) as nucleophiles. The reaction between bis(*OO'*-dimethyl dithiophosphate)nickel(II), $[Ni\{S_2P(OMe)_2\}_2]$, and 2,9-dimethyl-1,10-phenanthroline (dmphen) yielding the five-co-ordinate adduct has also been investigated.

The kinetics of the reactions were monitored in dry chloroform at 25·0 ± 0·1 °C using an Applied Photophysics stopped-flow device. The reactions were carried out under pseudo-first-order conditions with the entering nucleophile in excess. The nickel complexes were prepared as described in the literature[3,4] and they analysed satisfactorily.



SCHEME 1

The kinetic data for the reaction between $[Ni\{S_2P(OMe)_2\}_2]$ and dmphen are given by equation (1). This is consistent

$$k_{obs} = (97{\cdot}8 \pm 2{\cdot}3)[dmphen]\ s^{-1} \qquad (1)$$

with the associative mechanism shown in Scheme 1 which predicts the relationship shown in equation (2), in agreement

$$k_{obs} = k_1k_3[N\text{–}N]/(k_2 + k_3) \qquad (2)$$

with the experimental data (N–N = dmphen).

Conductivity measurements indicated that when $[Ni\{S_2P(OMe)_2\}_2(dmphen)]$ was treated with bipy and phen the charged $S_2P(OMe)_2^-$ rather than the neutral dmphen was displaced. The Figure shows plots of k_{obs} *vs.* nucleophile concentration for the reaction of bipy and phen with $[Ni\{S_2P(OMe)_2\}_2(dmphen)]$. The intercept is zero (within the experimental error) for the reaction of the substrate with phen and the second-order rate constant is given by equation (3).

$$k_{phen} = (24{\cdot}0 \pm 1{\cdot}2\ [phen]\ s^{-1} \qquad (3)$$

When bipy is the nucleophile, the k_{obs} *vs.* nucleophile concentration plots are linear with a small positive intercept (Figure). The magnitude of the intercept decreased from $(4{\cdot}0 \pm 0{\cdot}33) \times 10^{-2}\ s^{-1}$ to $(2{\cdot}0 \pm 0{\cdot}3) \times 10^{-2}\ s^{-1}$ when the concentration of dmphen present was increased from zero to ten-fold excess. The slope of the plots remained constant however, giving a value of $(4{\cdot}4 \pm 0{\cdot}1)\ dm^3\ mol^{-1}\ s^{-1}$ for k_{bipy}. The substrate concentration was varied between $6{\cdot}5 \times 10^{-5}$ and $1{\cdot}8 \times 10^{-4}\ mol\ dm^{-3}$ for both reactions. The addition of a ten-fold excess of dmphen had no effect on the values of k_{phen} and k_{bipy}. The standard errors quoted were calculated as described in the literature.[5]

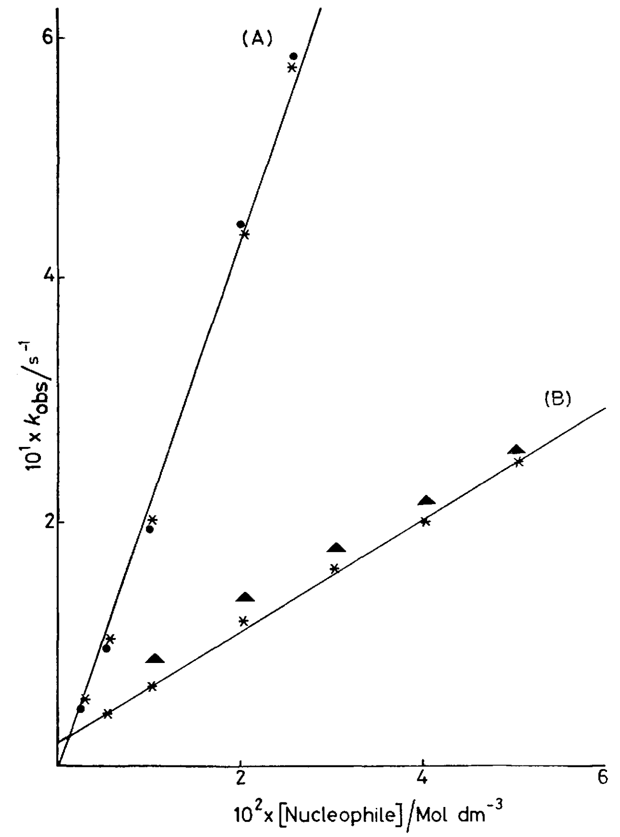
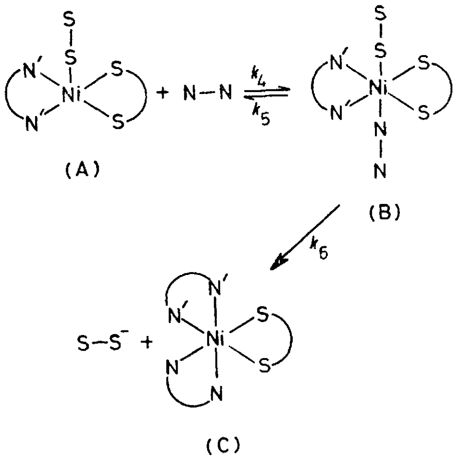


FIGURE. Kinetic results for the reactions of bipy and phen with $[Ni\{S_2P(OMe)_2\}_2(dmphen)]$ in chloroform at 25 °C. (A): Nucleophile = phen, $[Ni\{S_2P(OMe)_2\}_2\ (dmphen)] = 1{\cdot}8 \times 10^{-4}$ and $6{\cdot}5 \times 10^{-5}\ mol\ dm^{-3}$; ●, two-fold excess dmphen; ★ ten-fold excess dmphen. (B): Nucleophile = bipy, $[Ni\{S_2P(OMe)_2\}_2\ (dmphen)] = 1{\cdot}8 \times 10^{-4}$ and $6{\cdot}5 \times 10^{-5}\ mol\ dm^{-3}$; ▲, no excess dmphen; ★, ten-fold excess dmphen.

The intercept obtained in the bipy reaction appears to be due to a combination of a small dissociative contribution and the possibility that the reaction does not go to completion at low nucleophile concentrations. This is in agreement with the work of Grant and his co-workers[6] who found that the equilibrium constant for the reaction of $[Ni\{S_2P(OMe)_2\}_2]$ with bipy and phen was much larger for phen than for bipy.

The kinetic data are consistent with an associative mechanism in which bipy and phen react with the five-co-ordinate substrate (Scheme 2). Assuming (B) to be in a steady state, the reaction scheme predicts the relationship

$$k_{obs} = k_4k_6\ [N\text{–}N]/(k_5 + k_6). \qquad (4)$$



SCHEME 2. S–S = $S_2P(OMe)_2^-$; N–N = bipy or phen; N′–N′ = dmphen.

shown in equation (4). It is interesting that, contrary to what is usually observed,[7] k_{phen}/k_{bipy} = 5·5. Sweigart *et al.*[1b] obtained values ranging from 2·1 to 6·6 for the nucleophilic reactivity of phen relative to bipy with phosphine adducts of $[Ni\{S_2P(OR)_2\}_2]$. There are no obvious reasons for this because of the lack of correlation between kinetic and thermodynamic parameters for these systems.[6]

This study shows that substitution at 18-electron five-co-ordinate centres can proceed by an associative mechanism. Previous work suggested that these systems react exclusively by a dissociative mechanism. However, it appears that five-co-ordinate nickel(II) complexes in a suitable electronic environment, *e.g.* high-spin, can substitute *via* an associative mechanism.

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