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Cobalt–bisdipyridyl–nitrosyl Complexes. A Case of Reversible Redox Addition

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Cobalt(II)–bisdipyridyl complexes in presence of halide or nitrite ions react with nitric oxide with formation of $[Co(dipy)_2XNO]Y$ *(X = halide or nitrite ion,* $Y = ClO_4^-$, PF_6^-*). On the basis of infrared spectra, polarographic and magnetic behaviour it is assumed that the complexes contain the nitrosyl group in the* NO^- *form. In solution, a reversible equilibrium* $Co^{III}–NO^- \rightleftharpoons Co^{II} + NO$ *is established most probably via a* $Co^{II}–NO\cdot$ *species. Under mild conditions, the coordinated nitrosyl group is oxidized irreversibly to* NO^-_2*. Structural factors determining the observed behaviour are discussed.*

Introduction

It has been shown previously[1] that in the cobalt(II)–dipyridyl system the bis-complexes undergo the oxidation attack preferantially in such cases where redox addition mechanism might operate. Our interest in the redox addition reactions of d^7 systems led us to investigate the cobalt(II)--bisdipyridyl complexes in more detail. Among the reactions investigated, the reaction with nitric oxide was studied and we wish to report the results in the present paper.

Feltham and Nyholm[2] described the preparation of $[CoL_2XNO]^+$ complexes (L being ethylenediamine or *o*-phenylenebis(dimethylarsine)) by a reaction of the corresponding CoX_2L_2 species with nitric oxide, i.e. by a procedure which suggests a redox addition mechanism. The complexes prepared were stable in the solid state as well in the solution and are regarded to be $Co^{III}–NO^-$ species.

Furthermore, complexes of the type $[CoL_2(NO)](ClO_4)_2$ with L = ethylenediamine, *o*-phenylenediamine, or $[CoL_4(NO)]X_2$, with L = ethylenimine, pyridine and X = Cl^-, NO_3^- or ClO_4^-, were prepared[3] by the same general procedure.

On the basis of these results it could have been expected that the corresponding dipyridyl complexes would show an analogous behaviour. However, the investigation of the latter complexes has shown striking differences, especially as regards the conditions of the reaction with nitric oxide and the stability of the nitrosyl complexes formed, both towards oxidation and dissociation in the solution.

Experimental

Preparation of $[Co(dipy)_2Cl(NO)]ClO_4$

$CoCl_2 \cdot 6H_2O$ (0.5 g) and $LiClO_4 \cdot 3H_2O$ (0.4 g) were successively dissolved in 45 ml of absolute ethanol, the solution was deaerated by nitrogen and 0.65 g dipyridyl, dissolved in 5 ml of hot ethanol, was slowly added under nitrogen. Nitric oxide – washed with sodium hydroxide and sulphuric acid and passed through a trap at –78° – was bubbled through the solution under strong stirring for about 30 min. The brown, microcrystallinic solid formed was filtered off under nitrogen, washed with deaerated ethanol and ether and dried in vacuum. The samples were stored under nitrogen. All attempts to recrystallize the samples failed. Anal. Calcd. for $[Co(dipy)_2Cl(NO)]ClO_4$: C 44.85, H 3.00, N 13.03, Cl 12.8. Found*: C 44.83, H 3.12, N 12.66, Cl 12.58.

Preparation of $[Co(dipy)_2Cl(NO)]PF_6$

This compound was prepared by a procedure analogous to that for perchlorate using 0.74 g of $(Bu_4N)PF_6$ instead of $LiClO_4$. In this case a yellow precipitate is formed after addition of dipyridyl and nitric oxide was bubbled through the suspension. Anal. Calcd. for $[Co(dipy)_2Cl(NO)]PF_6$: C 41.2, H 2.76, N 12.0, Cl 6.0. Found: C 41.05, H 3.17, N 11.73, Cl 5.74.

Preparation of $[Co(dipy)_2(NO_2)NO]ClO_4$

$Co(NO_3)_2 \cdot 6H_2O$ (0.3 g) was dissolved in 10 ml of ethanol in a Schlenk tube, deaerated by nitrogen and dipyridyl (0.325 g) was added under strong stirring. In another Schlenk tube $NaNO_2$ (0.07 g) and $LiClO_4 \cdot 3H_2O$ (0.3 g) were dissolved in 20 ml of ethanol and deaerated. Both solutions were saturated with nitric oxide and mixed in NO atmosphere. The colour turned deep brown and precipitation of a yellowish brown solid immedi-

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* Analysis were performed in the Analytical Department of the Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences, Prague.

ately started. NO was bubbled through the stirred solution until the precipitation was completed. The resulting precipitate was filtered off under nitrogen, washed with deaerated ethanol and ether and dried in vacuum. The samples were stored under nitrogen. Anal. Calcd. for $[Co(dipy)_2(NO_2)(NO)]ClO_4$: C 43.95, H 2.93, N 15.39, Cl 6.4. Found: C 43.62, H 2.91, N 15.03, Cl 6.69. $[Co(dipy)_2(NO_2)(NO)]ClO_4$ kept under a layer of water on air for 2 months turns completely into $[Co(dipy)_2(NO_2)_2]ClO_4$, as was shown by the i.r. spectra and analysis. Anal. Calcd. for $[Co(dipy)_2(NO_2)_2[ClO_4$: C 42.70, H 2.85, N 14.94, Cl 6.24. Found: C 42.90, H 3.05, N 14.75, Cl 6.35.

Chemicals

Acetonitrile (LOBA Chemie) was repeatedly refluxed and distilled with P_2O_5. After the solvent remained colourless it was distilled from K_2CO_3 and fraction boiling at 81–81.5° used. Propylenecarbonate was a BDH product and was used directly after drying with NALSIT– 4 molecular sieve. All other chemicals were commercial materials, reagent grade (Lachema).

Magnetic susceptibilities were measured by the Gouy method or by the Faraday method in case of low temperature measurements. Varian E4–EPR spectrometer was used for measuring the EPR spectra. Infrared spectra were taken on a Perkin–Elmer Model 257 grating infrared spectrophotometer in KBr pellets or in solution using sealed 0.1 mm NaCl cells for both sample and reference. Unicam SP 800 was used for recording visible and UV spectra.

The solution from the reaction vessels were transferred to the spectrophotometric cells using the normal syringe technique. All measurements were carried out in cells completely filled with the solution to avoid any exchange of gases between the solution and the gas phase. The spectrophotometric cells were deaerated and filled with nitrogen or nitric oxide before filling with the sample.

Polarographic measurements at dropping mercury electrode were performed on a recording polarograph type LP–60 (Laboratorní přístroje, Praha). The multipurpose electrochemical cell[4] was used with the saturated calomel electrode as the reference electrode and platinum wire as the counter-electrode.

Results

Synthesis

The reaction between nitric oxide and cobalt(II)–dipyridyl (1:2) system is manifested by the appearance of a dark brown colour in the reaction mixture which takes place almost immediately after saturating the solution with nitric oxide. However, the very first experiments on the preparative scale indicated that the course of the reaction is rather complicated. When the reaction was carried out in the presence of chloride ions only, a small amount of precipitate was formed only after 24 hours at –30° C. The precipitate was a mixture of at least two compounds of irreproducible composition. When perchlorate or hexafluorophosphate were added to these solutions immediately *after* saturating them with nitric oxide, a brown precipitate was formed, the composition of which was, however, again hardly reproducible. Therefore perchlorate or hexafluorophosphate were added to the reaction mixture before saturating it with NO, in an attempt to precipitate immediately the compound when formed from the reaction mixture. If, however, perchlorate, hexafluorophosphate or nitrate were the only anions present no visible change of colour took place nor any precipitate was formed. The reaction between NO and cobalt(II)–dipyridyl complex takes place *only in presence of anions which can be incorporated into the coordination sphere* of the complex being formed. Halide ions and nitrite were shown to be most effective, in combination with perchlorate or hexafluorophosphate as anions in the outer sphere. Under these conditions, using rather dilute solutions and a prolonged bubbling of NO through the reaction mixture, the reaction proceeds to completion with a high yield of very pure complexes of the type $[Co(dipy)_2X(NO)]Y$, X being halide or nitrite, Y perchlorate or hexafluorophosphate.*

On the other hand when excess of dipyridyl is present no reaction with nitric oxide takes place at all. These purely preparative observations show that the only nitrosyl containing species which can be formed are bis-dipyridyl, six coordinate complexes and that nitrate or perchlorate are not capable to stabilize sufficiently the inner coordination sphere. This behaviour differs from that described by Feltham and Nyholm[2] who reported a species $[Co(en)_2(NO_3)(NO)](ClO_4)$ and in the case of $[Co(en)_2(NO)](ClO_4)_2$ assumed one of the perchlorate anions to be in the inner coordination sphere. However, Jackson *et al.*[3] regard complexes of the latter type as having coordination number 5. In the case of dipyridyl complexes *no evidence for the formation of stable five-coordinate complexes was found.* Furthermore, experiments carried out in solutions with more than two dipyridyl molecules per one cobalt atom show that reaction between cobalt(II)–dipyridyl complexes and nitric oxide proceeds only when nitric oxide can be incorporated into the coordination sphere, i.e. only by a redox addition and not by an electron transfer process.

Infrared Spectra

NO vibration

The infrared spectra of all the compounds prepared show only one absorption band at 1642 cm^{-1} attribut-

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* Similar reaction and analogous products are formed also when *o*-phenanthroline is used instead of dipyridyl.

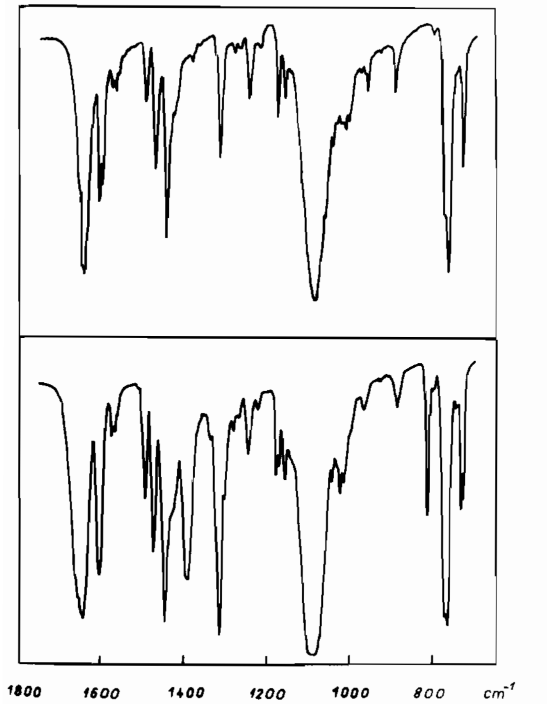

Figure 1. IR spectrum of $[Co(dipy)_2ClNO]ClO_4$ (a) and of $[Co(dipy)_2(NO_2)(NO)]ClO_4$ (b) measured in KBr pellets.

able to the NO stretching frequency (measured in nujol or KBr pellet). This characteristic absorption band is very strong and can be easily distinguished from the dipyridyl bands in the region round 1600 cm^{-1} (Fig. 1). In the case of the nitrosyl–chloro complex the NO band is sharp, whereas nitrosyl–nitro complexes show a broad band.

The observed NO stretching frequency falls into a region where it is rather difficult to distinguish unambiguously between NO^+ and NO^-.[6] In this particular region the frequencies of both bonding types of the NO ligand overlap. However, from the comparison with NO frequencies in analogous complexes (Table I), which were mostly formulated as containing the NO^- group,[7] it can be concluded that the cobalt–nitrosyl–dipyridyl complexes are to be formulated with the nitrosyl group in the NO^- form. The same NO frequency is observed also in fresh acetonitrile and propylenecarbonate solutions saturated with nitric oxide (see later).*

TABLE I. NO Vibrations in Some Cobalt–Nitrosyl Complexes.

Compound	ν_{NO}, cm^{-1}	Reference
$[Co(en)_2ClNO]ClO_4$	1611	2
$[Co(en)_2I\ NO]ClO_4$	1654	2
$[Co(en)_2NO](ClO_4)_2$	1663	2, 3
$[Co(das)_2ClNO]ClO_4$	1562	2
	1548[a]	2
$[Co(NH_3)_5NO]Cl_2$	1610	5
$[Co(dipy)_2ClNO]ClO_4$	1642	this work
$[Co(dipy)_2I\ NO]ClO_4$	1645	this work
$[Co(dipy)_2(NO_2)(NO)]ClO_4$	1642	this work

[a] Compound examined was a mixture of *cis* and *trans* isomers.

The identity of ν(NO) for chloro, iodo- and nitro-complexes points to the conclusion that the prepared complexes have most probably a *cis* configuration (configuration which seems to be most stable for bis-dipyridyl complexes for steric reasons[7]) and that the group *cis* to the NO ligand exerts only a very small *cis*-effect. The analogous ethylenediamine complexes[2] are formulated as having *trans* configuration and show a considerable dependence of ν(NO) upon the nature of the *trans* ligand.

NO_2 vibrations

NO_2 vibrations in $[Co(dipy)_2(NO_2)(NO)]ClO_4$ are located at 1390 cm^{-1} (strong), 1312 cm^{-1} (strong, coinciding with m band of dipyridyl at 1320 cm^{-1}) and at 814 cm^{-1} (medium, sharp). These bands are well in the region of NO_2^- ligands and exclude the possibility of ONO^- configuration.

The dipyridyl bands are similar to those of other complexes of the cobalt(III)–bisdipyridyl series.

Magnetic Properties

As can be seen from Table II all compounds prepared are slightly paramagnetic. The EPR spectra, however, show only very weak and broad absorption. The values of χ_{corr} follow the Curie–Weis law with the Weis constant of 43° K. The temperature-independent paramagnetism being thus excluded, we have to consider other sources of paramagnetic behaviour. The method of preparation does not exclude the possibility of contamination of the samples by small amounts of strongly paramagnetic cobalt(II) impurities. However, the measured magnetic susceptibility was constant for several samples prepared independently. High temperature-dependent paramagnetism has been described for cobalt(III) oxalate (μ = 1.37 B.M., Θ = 79° K)[8] and for $Co(indenyl)_2^+$ (μ_{eff} = 1.76).[9] If contamination with cobalt(II) impurities would be excluded, the observed behaviour could result from a low-lying paramagnetic excited state. This hypothesis is being followed experimentally on a series of cobalt(III)–bisdipyridyl complexes and the results will be reported in due time.

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* It has to be noted, that in the infrared spectra of KBr pellets, which were prepared on air with prolonged grinding, a sharp band at 1382 cm^{-1} appears without any substantial decrease in the intensity of the 1642 cm^{-1} band. The same band appears also in some decomposition products. This region is typical for NO_2^- vibrations, however, other bands typical for NO_2^- ligands are missing.

TABLE II. Magnetic Properties of $[Co(dipy)_2X\ NO]Y$ Complexes.

Complex	T(° K)	$\varkappa$ (cgs units)	χ_{corr}[a]	μ_{eff} (B.M.)
$[Co(dipy)_2ClNO]PF_6$	298	0.428×10^{-6}	525×10^{-6}	1.14
$[Co(dipy)_2ClNO]ClO_4$	298	0.870×10^{-6}	638×10^{-6}	1.24
	273	0.970×10^{-6}	678×10^{-6}	1.22
	196	1.480×10^{-6}	881×10^{-6}	1.18
	77	3.870×10^{-6}	1831×10^{-6}	1.07
$[Co(dipy)_2(NO_2)(NO)]ClO_4$	298	0.908×10^{-6}	653×10^{-6}	1.25

[a] Calculated using the measured value of d = 1.34 g/cm^3; diamagnetic correction calculated by the use of data given in "Modern Coordination Chemistry" (J. Lewis and R.G. Wilkins editors), Interscience, New York, N.Y., 1960.

Solution Properties

All compounds prepared are insoluble in water, methanol and ethanol. They dissolve very easily in acetone, acetonitrile and propylenecarbonate.

The solutions in acetonitrile and propylenecarbonate are not stable. Infrared and visible spectra as well as the polarographic behaviour of the solutions indicate that nitric oxide and cobalt(II)-bisdipyridyl complexes are formed rapidly on dissolution. When, however, the solvent is saturated with nitric oxide before dissolving the complex, no decomposition takes place. When nitric oxide is removed from these solutions by bubbling nitrogen, the formation of cobalt(II)–bisdipyridyl takes place. This process is reversible, i.e. saturation of such a solution with nitric oxide results in the formation of the nitrosyl complex and the process can be repeated several times.

These results show that an equilibrium is established in the solution,

$$Co^{III}\text{–}NO^- \rightleftarrows Co^{II} + NO \qquad (1)$$

Experimental evidence shows that in propylenecarbonate this equilibrium is shifted almost completely to the right side even without removing nitric oxide by nitrogen and is established very rapidly. In acetonitrile the attainment of the equilibrium is much slower and is completed only when nitric oxide is removed continuously by nitrogen. The establishment of this equilibrium (which proceeds even in dichloromethane, however, under complete destruction of the complex) makes the recrystallization of the samples impossible and the preparative procedure completely understandable.

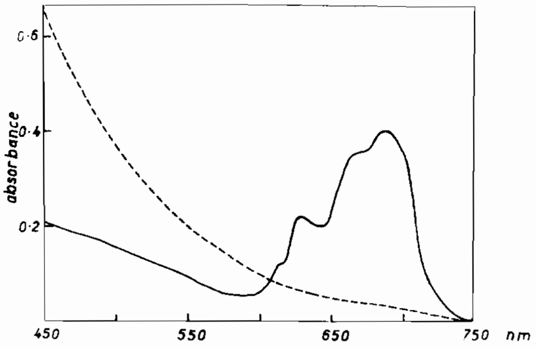

Figure 2. Decomposition of $[Co(dipy)_2ClNO]ClO_4$ in solution. Dashed line: visible spectrum of $5 \times 10^{-3}M$ solution in propylenecarbonate, saturated with NO. Solid line: visible spectrum of the same solution without saturating with NO. This curve is almost identical with that of the solution of $CoCl_2$ ($5 \times 10^{-3}M$) and dipyridyl ($10^{-2}M$) in propylenecarbonate.

The reversible nature of the redox addition process is shown also by the influence of excess of dipyridyl upon the solution of the complexes. Polarographic evidence shows that in presence of excess of dipyridyl the compounds dissolve with complete formation of cobalt(II)–trisdipyridyl complex.

This reversibility of the redox addition process is the most striking difference between the bisdipyridyl and bisethylenediamine series. In the latter case,[2] the complexes can be recrystalized without decomposition, i.e. no considerable dissociation of nitric oxide takes place in the solution of bisethylenediamine complexes.

The polarographic behaviour cannot be followed directly due to the decomposition described above. However, indirect evidence was found using the fact that the cobalt(II)–bisdipyridyl complexes react rapidly with nitric oxide: $[Co(dipy)_2(NO_2)_2]^+$ in dry propylenecarbonate is reduced at the dropping mercury electrode in a one-electron, reversible wave with $E_{1/2} = -0.05$ V (in $0.1M$ $LiClO_4$ vs aqueous saturated calomel electrode), i.e. $[Co(dipy)_2(NO_2)_2]$ is formed primarily as the product of the electrode reaction. When nitric oxide in stoechiometrically comparable concentration is added to the solution, the original wave of $[Co(dipy)_2(NO_2)_2]^+$ shifts towards more positive potentials by about 100 mV and a new wave appears at −0.18 V (vs aqueous SCE). No wave of free nitric oxide at −0.4 V is observed. The new wave is diffusion–controlled. Using the standard polarographic criteria,[10] the following mechanism can be deduced on the basis of these results:

$$\begin{tikzcd}
{[Co^{III}(dipy)_2(NO_2)_2]^+} \arrow[r, shift left, "-0.05\ V"] & {[Co^{II}(dipy)_2(NO_2)_2]} \arrow[l, shift left] \arrow[dl, bend left, "NO"] \\
{[Co(dipy)_2NO(NO_2)]^+} \arrow[r, "-0.18\ V"] & (Co^{II}) \arrow[l, bend left, "NO"]
\end{tikzcd} \qquad (2)$$

i.e. the product of the reduction in the first wave is reoxidized with nitric oxide under the formation of a complex of trivalent cobalt having, however, different composition from the original depolarizer. The chemical evidence points to the conclusion that the reaction with nitric oxide proceeds only with the incorporation of NO into the coordination sphere so that the wave at −0.18 V can be ascribed to the reduction of $[Co(dipy)_2NO(NO_2)]^+$. An almost identical behaviour was observed when starting with $[Co(dipy)_2Cl_2]^+$ and $[Co(dipy)_2CO_3]^+$ instead of with $[Co(dipy)_2(NO_2)_2]^+$.

Stability in the Solid State

$[Co(dipy)_2Cl(NO)]$ –hexafluorophosphate and –perchlorate are stable when under nitrogen or vacuum even if heated for several hours to 100° C.

On air, however, the hexafluorophosphate salt turns in few days into a red-violet crystaline material. At the same time, the typical NO infrared band at 1642 cm^{-1} disappears completely and new bands at 1500 cm^{-1}, 1430 cm^{-1}, 1381 cm^{-1}, 1285–1265 cm^{-1} (group of bands) are formed. There is no change in the magnetic susceptibility of the material. The analysis suggests the composition $[Co(dipy)_2Cl(NO_2)]PF_6$ (found: C 40.39, H 2.89, N 11.73, Cl 5.56; calcd.: C 40.30, H 2.68, N 11.70, Cl 5.58). The infrared evidence shows, however, that the material is a mixture, most probably of NO_2^- and ONO^- complexes.

The perchlorate undergoes the same process, however, much more slowly. The conversion can be accelerated by heating the sample on air at 100° C for several hours. Under these conditions a partial splitting of NO takes place and a part of cobalt is converted into the divalent state, as manifested by the increase of magnetic susceptibility of the sample.

The $[Co(dipy)_2(NO_2)NO]ClO_4$ is stable when kept under nitrogen at normal temperature. Heating under nitrogen or vacuum results in the loss of NO and decomposition of the sample. Long standing of the sample on air or heating to 100° C on air for several hours results in partial oxidation to $[Co(dipy)_2(NO_2)_2]ClO_4$, as manifested by the appearance of the infrared band at 1420 cm^{-1} and a doublet at 811 cm^{-1} and 821 cm^{-1} (cf. Ref. 1). Partially, however, NO is also lost under the formation of divalent cobalt ($\varkappa$ of the sample increases from 0.9×10^{-6} to 7.8×10^{-6} cgs unit) and the infrared spectrum shows bands attributable to mono-NO_2 complexes and bands which can be ascribed to bridging NO_2^- groups (1515 cm^{-1}, 1200 cm^{-1}, 970 cm^{-1}; cf. Ref. 11 with 1485 cm^{-1} and 1183 cm^{-1} for the bridging NO_2^- group).

Pure $[Co(dipy)_2(NO_2)_2]ClO_4$ can be obtained from the corresponding nitrosyl species only by a very slow oxidation, e.g. by storing the solid $[Co(dipy)_2(NO_2)NO]ClO_4$ under a layer of water for two months.

The essential conclusion from these observations is that coordinated NO can be oxidized to NO_2^- in the solid state, however, only at very mild conditions, otherwise partial decomposition under the loss of NO takes place. This loss of NO is much more pronounced with the NO_2 complexes, probably due to the ability of the NO_2^- ligand to substitute the NO group under the formation of a bridge. The solid state behaviour shows thus a pattern similar to that of the behaviour in the solution: the NO ligand can be lost easily supposing another ligand is able to enter the coordination sphere.

Discussion

As already mentioned, the infrared as well as the polarographic evidence point to the conclusion that the $[Co(dipy)_2XNO]^+$ complexes are to be formulated with the nitrosyl group in the NO^- form. The magnetic behaviour and other properties support this formulation. The coordinated nitrosyl group can be, under mild conditions, oxidized by air to the NO_2^- group. This process is, however, irreversible as the corresponding nitrite complexes are not converted into the original nitrosyl complex upon the influence of strong acid.* This indicates that the coordinated nitrosyl group does not behave chemically as the NO^+ group.

The very easy and reversible decomposition in the solution under the formation of nitric oxide and cobalt(II) complexes (as well as the reaction with excess dipyridyl) suggests that there is only a relatively small energetic difference between the $Co^{III}–NO^-$ and $Co^{II}–NO\cdot$ configurations. On the basis of chemical behaviour, it can be assumed that the equilibrium

$$Co^{III}–NO^- \rightleftarrows Co^{II}–NO\cdot$$

is primarily established in the solution. This equilibrium is most probably shifted to the left hand side. However, the $Co^{II}–NO\cdot$ form is very labile as regards substitution and splits off nitric oxide. In this way the equilibrium is distorted and, in absence of excess of nitric oxide, the complete formation of cobalt(II)–bisdipyridyl complexes results.

The NO^- form is generally preferred in such cases where the remaining part of the complex is strongly basic. This is, however, not the case with dipyridyl molecules in the coordination sphere. The electron withdrawing effect of dipyridyl molecules makes the $Co(dipy)_2X$ unit only weakly basic and the interaction of metal π-orbitals with $\pi^*(NO)$-orbitals would be relatively small. The latter orbitals are obviously of slightly lower energy to the d_{z^2} or $d_{x^2-y^2}$ orbitals of cobalt(II) so that electron transfer from these metal orbitals into the $\pi^*(NO)$ orbitals takes place. On electron transfer to the NO, the decrease of Co–N–O bond angle takes place and the interaction of the $\pi^*(NO)$ and metal d_{z^2}

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* Unpublished results; cfr. also the method of preparation of $[Co(dipy)_2(NO_2)_2]^+$ complexes described previously.[1]

orbitals is possible[12] stabilizing the new electron configuration. The primary interaction of metal π-orbitals with π^*(NO)-orbitals being, however, rather weak the resulting differencies in orbital energies are presumably small so that the electron correlation effects determine the resulting electron configuration to a great extent. This effect explains the relatively small energy difference between the low spin, Co^{III}–NO^-, and high-spin Co^{II}–$NO\cdot$ configurations, suggested by the chemical behaviour.

It is known (cf. e.g. Ref. 13) that the NO^- group exerts a strong *trans*-effect. In the case of ethylenediamine complexes, for which a *trans* configuration is assumed, this high *trans*-effect might result in the formation of penta-coordinated complexes. In the case of dipyridyl complexes, having most probably a *cis* configuration, the *trans*-effect of the NO^- group is exerted upon the rather strongly bound dipyridyl which does not get split off so that penta-coordinated species are not formed in the bisdipyridyl series. The great *trans*-effect of the NO^- group which cannot be realized, might also contribute to the instability of the Co^{III}–NO^- configuration.*

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* *Note added in proof:* One of the referees suggested the possibility that the complexes described might have a distorted *trans* configuration. There is, of course, no direct evidence for the *cis* arrangement we assume. However, all the behaviour described is fully compatible with such configuration and the solution properties are fully understood when *cis* configuration is assumed.

The distorted *trans* configuration would be expected to show the opposite tendency in solution, i.e. the splitting off of the ligand *trans* to the NO group due to the very large *trans*-effect of the NO^- group (cf. D. A. Snyder and D. L. Weaver, *Chem. Comm.,* 1425 (1969)). Furthermore, the tendency to be converted into the limiting case of such a distorsion, i.e. trigonal bipyramid, would be expected. However, no evidence for such a behaviour was observed.