# The Influence of *trans*-Ligands on the Co–NO$_2$ Bond Length in Mixed Cobalt(III) Complexes

By Rajna Herak
(*Laboratory of Solid State Physics and Radiation Chemistry, 'Boris Kidrič' Institute,* 11001 *Belgrade, P O Box* 522, *Yugoslavia*)

and Nenad Juranić* and Milenko B Ćelap
(*Institute of Chemistry, Faculty of Sciences, University of Belgrade,* 11001 *Belgrade, P O Box* 550, *Yugoslavia*)

*Summary* An *X*-ray crystal structure investigation of 12 cobalt(III) complexes has shown that the Co–NO$_2$ bond length is shorter by an average of 0·05 Å when *trans*-to carboxylato-oxygen than when *trans*- to a nitrogen ligator

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From *X*-ray crystal structure investigations reported for twelve cobalt(III) complexes (see the Table), which, besides other ligands, contain NO$_2^-$ group(s), we have observed the influence of *trans*-ligands on the Co–NO$_2$ bond length In 6 compounds, containing amino acid carboxylato-oxygen *trans* to the NO$_2^-$ group, the Co–NO$_2$ bond length is shorter by an average of 0·05 Å than the same bond when *trans* to ammonia, the NO$_2^-$ group, or the amino nitrogen of aminocarboxylato and diamine ligands (Table) This influence is not noticeable in other Co–ligand bonds, *i e* Co–NH$_3$, Co–NH$_2$ (amino acid), Co–NH$_2$ (diamine), and Co–O (amino acid) In this way the Co–NO$_2$ bond length appears to be especially sensitive to a carboxylato-oxygen in a *trans*-position

The nature of the NO$_2^-$ ligand bonding in octahedral complexes is not completely understood and seems to differ considerably from that in square-planar complexes In the square-planar complexes the NO$_2^-$ ligand position in the spectrochemical series,[1] as well as its pronounced *trans*-effect,[2–4] indicate that a considerable electron density back-donation from the metal d$_\pi$-orbital to a vacant $\pi$-antibonding orbital of the NO$_2^-$ group occurs [5] In contrast with this, in octahedral complexes the *trans*-effect of the NO$_2^-$ group is weakly pronounced[3] and this has been explained in terms of a difficulty in $\pi$-bond formation due to steric effects However, the biphilicity of the NO$_2^-$ group observed during octahedral substitution reactions[6] shows that $\pi$-bond participation in the NO$_2^-$ group–metal bonding also occurs in octahedral complexes Therefore, the observed influence of carboxylato-oxygen, in a *trans*-position, on the Co–NO$_2$ bond strength might be significant when considering the importance of the $\pi$-bonding of the NO$_2^-$ group in octahedral complexes The observed *trans*-influence can be explained well by $\pi$-bonding participation in Co–NO$_2$ bond formation The carboxylato-oxygen, as a $\pi$-donor, allows the d$_\pi$-orbitals to become antibonding to some extent, leading to the destabilization of the complex In that case, the formation of the $\pi$-bond between the metal and the NO$_2^-$ ligand in a *trans*-position to the

TABLE. The dependence of the Co–$NO_2$ bond length (Å) in the investigated complex on the ligand in a *trans*-position and the corresponding angles (°) of the mean plane of the $NO_2$ group to the principal axes of the complex.

| | Co–$NO_2$ bond length (Å) *trans*- to | | | | | |
|---|---|---|---|---|---|---|
| Complex | O | $NO_2$ | $NH_2$ | $NH_3$ | Angle (°) | Reference |
| *trans,trans,trans*-$K[Co(\beta\text{-ala})_2(NO_2)_2]$[a] | | 1·940(10) | | | 90·4 | 8 |
| $(-)_{589}$-*trans*-$(NO_2,NH_2)$-*trans*-*N*-$[Co(\text{L-his})_2NO_2]\cdot H_2O$[b] | | | 1·954(12) | | 16·5 | 9 |
| *trans*-$[Co(tn)_2(NO_2)_2]NO_2$[a] | | 1·926(6) | | | 91·4 | 10 |
| $(+)_{589}$-*trans*-$(NO_2,NH_2)$-$Ba[Co(glygly)$-$(\text{D-ala})NO_2]Cl\cdot 4H_2O$ | | | 1.936 | | 34.8 | 11 |
| *trans*-$[Co(tn)(\beta\text{-ala})(NO_2)_2]$ | | 1·912(5) | | | 88·0 | 12 |
| | | 1·980(6) | | | 85·5 | |
| *cis*-$(NO_2)$-*mer*-$(NH_2)$-$[Co(tn)(\beta\text{-ala})(NO_2)_2]\cdot H_2O$ | 1·892(4) | | 1·937(4) | | 35·1 | 13 |
| *cis*-$(NO_2,NH_3)$-*trans*-$(NH_2)$-$[CoNH_3(gly)_2NO_2]\cdot H_2O$ | 1·875(7) | | | | 35·5 | 14 |
| $(+)_{589}$-*cis*-$(NO_2)$-*trans*-$(NH_3,NH_2)$-$[Co(NH_3)_2(\text{L-ala})(NO_2)_2]$ | 1·894(2) | | | 1·942(3) | 40·1 | 15 |
| *mer*-*trans*-$(NH_3,NH_2)$-$K[Co(NH_3)(gly)(NO_2)_3]\cdot H_2O$ | 1·891(7) | 1·920(7) | | | 3·6 | 16 |
| | | 1·929(7) | | | | |
| $(+)_{589}$-*cis*-$Ag[Co(\text{D-ala})_2(NO_2)_2]$[a] | 1·87(2) | | | | 32·1 | 17 |
| *cis*-$[Co(tn)_2(NO_2)_2]Cl\cdot H_2O$ | | | 1·924(3) | | 34·5 | 18 |
| | | | 1·936(3) | | 35·3 | |
| $(+)_{589}$-*cis*-$[Co(\text{L-arg})_2(NO_2)_2]NO_3\cdot 2H_2O$ | 1·894(7) | | | | 35·4 | 19 |
| | 1·941(7) | | | | 32·4 | |

[a] The complex ion has an element of symmetry ($\bar{1}$ or 2). [b] *N* is the nitrogen atom belonging to the imidazole ring. alaH = alanine; hisH = histidine; tn = 1,3-diaminopropane; glyglyH$_2$ = glycylglycine; glyH = glycine; argH = arginine.

carboxylato-oxygen is favoured, since the electron density shifts through the $d_\pi$-orbitals to the vacant $\pi$-antibonding orbital of the $NO_2^-$ ligand. Therefore, the participation of the $\pi$-bond could be expected to be more pronounced and the Co–$NO_2$ bond length to be shorter when the $NO_2^-$ ligand is *trans* to a carboxylato-oxygen than when it is *trans* to a $\sigma$-bonded nitrogen. A corresponding bond length shortening has actually been observed, indicating $\pi$-bond participation in $NO_2$ bonding in $Co^{III}$ complexes. However, in all the compounds the mean plane of the $NO_2^-$ group when *trans* to the carboxylato-oxygen (and also in many other cases) is inclined to the principal axis of the complex at an angle of 30—40° (Table). Thus the possibility of $\pi$-bond formation with $d_\pi$-orbitals is reduced, though not excluded.[7] The shifting of the electron density from carboxylato-oxygen through the metal $d_\pi$-orbitals to the vacant $\pi$-antibonding orbital of the $NO_2^-$ ligand should have been reflected also in lengthening of the N–O bonds. There is no detectable evidence for this from the *X*-ray crystallographic data, however.

On the basis of the above, there is no straightforward conclusion as to the character of the M–$NO_2$ bond in octahedral complexes. The observed $NO_2^-$ ligand characteristics are most likely determined by a competition between the tendency for $\pi$-bond formation and the steric influences of the *cis*-ligand.

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