

The anisotropic π -effect of the nitro group in ammine–nitro cobalt(III) complexes

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Abstract—The analysis of crystal structures of the series of ammine–nitro cobalt(III) complexes has shown that Co—NO₂ bond lengths can be successfully rationalized on the basis of the anisotropic π -effect of nitro groups. This effect governs both the orientation of the nitro group and the Co—NO₂ length, and explains the irregularities in the increase of the latter with the increasing number of NO₂ groups present in the coordination sphere. © 1997 Elsevier Science Ltd

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The complexes containing anisotropic metal–ligand bonds have been for a long time the subject of our interest [1]. We have accumulated evidence that the so called *mutual influence of ligands* [2,3] though the central metal atom manifests itself in a stereochemically specific way if the metal–ligand bond is anisotropic. For this phenomenon we propose the term *anisotropic π -effect* [4]. The anisotropic π -effect is based on the known fact that sharing of the same *d*-orbital by two or more ligands for π -bonding is energetically unfavourable [8–10].

Two principal consequences of the anisotropic π -effect are that the anisotropic ligands tend to take mutual positions and orientations in which the least number of ligand π -orbitals will share the same metal *d*-orbital capable of π -bonding. Second, in cases where other factors (such as hydrogen bond formation or crystal packing forces) dominate the stereochemistry and hinder the most favourable ligand orientation forcing two or more ligand π -orbitals to share the same *d*-orbital, the anisotropic π -effect manifests itself through an increase in metal–ligand bond lengths.

In this work the Co—NO₂ lengths of the almost [11] complete series of ammine–nitro cobalt(III) complexes [Co(NH₃)_{6-n}(NO₂)_n]³⁺ (*n* = 1, . . . 6), are analysed and rationalized on the basis of the proposed anisotropic π -effect of nitro groups.

EXPERIMENTAL

All structures containing cobalt(III) and nitro groups were retrieved from the Inorganic Crystal Structure Database (ICSD) [12]. From the initial set of 34 hits, 11 structures were excluded either because they contained bridging NO₂⁻ ligands, or unidentate NO₂⁻ coordinated through oxygen, or other ligands (besides NO₂⁻ and NH₃) in the coordination sphere. The usual procedure of screening on the basis of the crystallographic *R*-factor was not performed due to the small total number of hits. So, the remaining set of 23 structures was screened manually whereupon the following three structures were left out: K[Co(NO₂)₄(NH₃)₂] [13] which did not contain the atomic positions for the NO₂ groups; Ag[Co(NH₃)₂(NO₂)₄] [14] due to the error in coordinates; and [Co(NH₃)₃(NO₂)₃] [15] which was claimed to be wrong and redetermined by Laing and coworkers [16]. Furthermore, an old powder diffraction result for a hexanitrocobaltate(III) salt [17] was substituted by the accurate recent results [18,19] of one of the authors. Finally, two more structures, which were not found in ICSD, were included in this survey (Table 1): the structure of *trans*-[Co(NH₃)₄(NO₂)₂]⁺ reported by Cagnon [20] and another structure of *trans*-[Co(NH₃)₂(NO₂)₄] by Bernal [21].

It should be pointed up that all hits in the ICSD were commented with the statement that 'the atomic

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Table 1. The Co—NO₂ bond lengths in the crystal structures of ammine-nitro complexes of cobalt(III) (in Å) as reported in the cited publications

Complex	Bond length	Ref.
[Co(NH ₃) ₅ (NO ₂) ²⁺	1.912(14)	[40]
	1.92(1)	[41]
	1.92(2)	[42]
	1.926(4)	[43]
	1.922(6)	[43]
<i>trans</i> -[Co(NH ₃) ₄ (NO ₂) ₂] ⁺	1.883(18) ^a	[43]
	1.933(11)	[44]
	1.937(11)	
	1.941(3)	[20]
<i>cis</i> -[Co(NH ₃) ₄ (NO ₂) ₂] ⁺	1.932(3)	
	1.900(15) ^a	[45]
<i>mer</i> -[Co(NH ₃) ₃ (NO ₂) ₃]	1.948(14)	
	1.92(1)	[16]
	1.90(1)	
<i>fac</i> -[Co(NH ₃) ₃ (NO ₂) ₃]	1.93(1)	
	1.945(13)	[46]
	1.904(14)	
	1.907(16)	
	1.958(12)	[46]
<i>trans</i> -[Co(NH ₃) ₂ (NO ₂) ₄] ⁻	1.918(20)	
	1.880(17)	
	1.96 ^b	[24]
	1.96 ^b	
	1.96 ^b	
	1.96 ^b	
	1.956(9)	[47]
	1.946(9)	
	1.964(9)	
	1.927(9)	
	1.959(3)	
	1.933(3)	
	1.942(4)	
	1.954(4)	
	1.935(3)	[21]
	1.945(4)	
	1.961(4)	
1.972(4)		
1.970(11)	[25]	
1.937(9)		
1.979(11)		
1.969(13)		
1.949(14)	[25]	
1.898(11)		
1.949(14)		
1.951(12)		
1.939(6)	[49]	
1.919(8)		
1.928(7)		
1.958(7)		
[Co(NO ₂) ₆] ³⁻	1.9516(7)	[50]
	2.040 ^c	[27]
	2.102 ^c	[27]
	2.070 ^d	[17]
	1.98(8)	[51]
	1.9639(3) ^e	[18]
1.966(1) ^f		

Table 1. Continued

Complex	Bond length	Ref.
	1.9610(2) ^g	[19]
	1.9655(2) ^h	

^a Excluded on the basis of the *Q*-test.^b No e.s.d.s reported in the paper.^c Old data; excluded from the analysis on the basis of the *Q*-test.^d Old powder diffraction result; new results (refs. 18 and 19) used instead.^e Measured at 113 K.^f Measured at 293 K.^g IAM refinement (see ref. 19.)^h Multipole refinement (see ref. 19.)

distances do not agree with those calculated during the testing' and that 'atomic coordinates are probably correct'. Therefore, we have recalculated Co—NO₂ bond lengths in each structure from the reported atomic coordinates (with PARST [22] ORTEP [23], as well as with locally written programs). Very small differences between reported and recalculated Co—NO₂ bond lengths were found only in two [Co(NH₃)₂(NO₂)₄]⁻ structures [24,25] but they did not affect the results of the present work.

Figure 1 shows weighted mean values of (reported) Co—NO₂ bond lengths together with the intervals for the reported values. An almost identical graph follows from the recalculated Co—NO₂ distances. Among

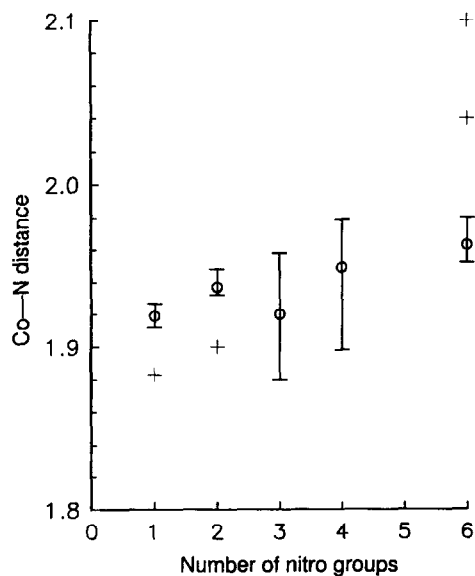


Fig. 1. The distribution of the Co—NO₂ distances in the crystal structures of [Co(NH₃)_{6-n}(NO₂)_n]³⁻ⁿ (*n* = 1, ... 6) series of complexes assorted according to the number of the NO₂ groups present in the coordination sphere. Open circles represent weighted mean values and the vertical bars show the ranges of bond lengths (min—max); crosses indicate the rejected values on the basis of Dixon's *Q*-test (*P* = 0.05).

mononitro and dinitro structures there were two rather short Co—NO₂ distances (see Table 1) which were treated as statistical outliers on the basis of the Dixon's *Q*-test (with *P* = 0.05) [26] and were excluded from Fig. 1. Also the very long Co—NO₂ bonds in old reports for ammonium and potassium hexanitrocobaltates [27] (2.04 and 2.10 Å, respectively) were excluded on the basis of the same criterion [28].

RESULTS AND DISCUSSION

The coordination of the nitro group has been extensively studied by different authors using various methods [29–34]. The position of the nitro group in the spectrochemical series [35], the tendency of different metals to form nitro as opposed to nitrito complexes [29,30] trans-effect of the nitro group [5,29,30,36,37], and shortening of Co—NO₂ bond when a carboxylato oxygen occurs in the trans-position [38] all point to the π -acceptor rôle of the NO₂ ligand. It is due to a weak but discernible interaction of the 2b₂ LUMO of the NO₂ ligand with the corresponding t_{2g} metal orbital (an EHMO [39] representation of which is shown in Fig. 2).

In all known crystal structures of the complexes in the series [Co(NH₃)_{6-n}(NO₂)_n]³⁻ⁿ, (*n* = 1, . . . 6) (Table 1), except in some [Co(NO₂)₆]³⁻ salts, the main binding forces between molecules are intermolecular N—H . . . O hydrogen bonds. These as well as the intramolecular hydrogen bonds determine the orientation of the nitro groups. Therefore the mutual influence of nitro ligands can be seen only from the differences in bond lengths.

The lengths of the Co—NO₂ bonds in ammine-nitro complexes increase with increasing number of nitro groups present in the coordination sphere (Table 1), but in a markedly irregular way (see Fig. 1). The plausible explanation of this relationship, on the basis of the anisotropic π -effect of nitro groups, is as follows.

In complexes with only one NO₂ group, there is no anisotropic π -effect, and the Co—NO₂ bonds are

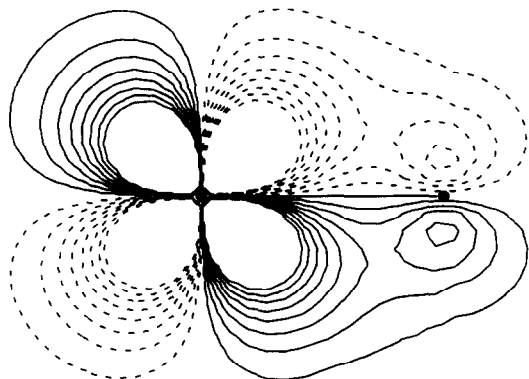


Fig. 2. EHMO [39] produced contour plot of the π -orbital of the coordinated NO₂ group, responsible for the anisotropic π -effect, on the plane perpendicular to the NO₂ group.

relatively short. In all known crystal structures nitro groups are oriented such that the plane containing NO₂ atoms bisects the angle of the coordinate axes perpendicular to the Co—NO₂ bond. This orientation maximizes the intramolecular hydrogen bonding.

In both *trans*-dinitro complexes NO₂ groups are coplanar (also in a plane which bisects the angles of the coordinate axes perpendicular to the NO₂—Co—NO₂ axis; see Fig. 3a). Their out-of-phase combination interacts with one metal t_{2g} orbital (say, a 1/√2(|xz⟩ + |yz⟩) linear combination). As a consequence, the Co—NO₂ bonds are longer than in mononitro complexes.

In the *cis*-dinitro complex NO₂ groups are oriented in a disrotatory way (in the Woodward–Hoffmann sense; see Fig. 3b). This conformation enables all three metal t_{2g} orbitals to be involved in metal–ligand π -interactions, so we have (at least one) noticeably short Co—NO₂ bond.

Looking at the orientations of the nitro groups in the complexes containing three nitro groups (Fig. 3c,d) it is noticed that the π -bonding involves all three metal t_{2g} orbitals. Accordingly, three ligand π -orbitals share three metal *d*-orbitals. Therefore, the bond lengths are closer to those found in mononitro complexes, or generally shorter than those observed for *trans*-dinitro complexes.

For tetranitro complexes only the *trans* isomers are crystallographically characterized. Practically in all reported structures the NO₂ groups are inclined with respect to the equatorial plane of the complex anion in a conrotatory fashion. In this way, all three cobalt t_{2g}-orbitals are involved in π -bonding, although not uniformly (Fig. 3e,f): the one defined with respect to the equatorial plane is involved more than the other two. Consequently, four ligand orbitals share less than three metal orbitals (since two other metal t_{2g}-orbitals are only partly involved), and the Co—NO₂ bond lengths are expected to be longer than in the case of trinitro complexes, as it is indeed observed.

No crystal structure of a pentanitro complex has been reported. The Co—NO₂ bonds in hexanitrocobaltate(III) complexes are long, as may be expected. In these structures six ligand orbitals share three metal orbitals irrespective of their orientation, although in all known examples the structures possess regular T_h symmetry. The lack of intramolecular hydrogen bonding in these structures is probably the reason why none of the NO₂ groups adopts a skew orientation with respect to the coordinate axes defined by the metal–ligand bonds (as invariably observed in all the above mentioned nitro-ammine complexes).

We argue that the anisotropic π -effect is an important conformation determining factor, together with the hydrogen bonding, but more important than any intramolecular steric effect. A corroboration for the latter comes from the Monte Carlo simulated annealing study of the stereochemistry of [Co(NO₂)₆]³⁻ which shows that the barrier for the rotation about the Co—NO₂ bond is less than 1 kcal/mol per NO₂

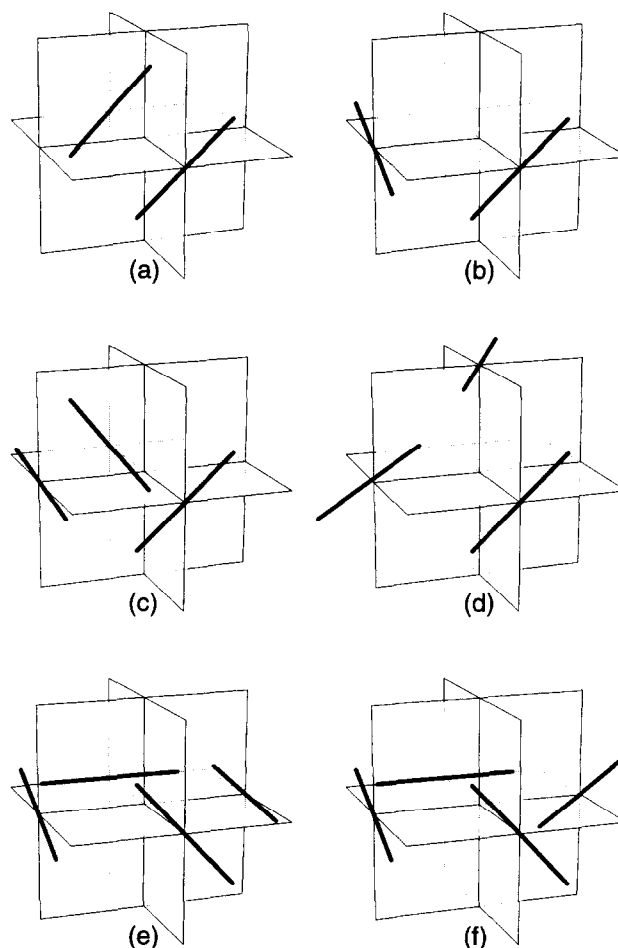


Fig. 3. Simplified pictorial representation of the observed orientations of the NO_2 π -acceptor orbitals (thick lines) with respect to the metal t_{2g} orbitals (specified by three mutually perpendicular planes): (a) trans-dinitro; (b) cis-dinitro; (c) meridional trinitro; (d) facial trinitro; and (e,f) two modes of orientations found in trans-tetranitro complexes of the $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]^{3-n}$, ($n = 1, \dots, 6$) series.

group [52]. Therefore, intramolecular steric effects are very likely to play a minor rôle in determining the orientation of the coordinated nitro groups.

The analysis reported here may prove to be of value, through assessing of the relative importance of steric effects (including the hydrogen bonding) and of electronic effects (in the form of the anisotropic π -effect of the nitro groups), in rationalizing variations of other related properties in the $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]^{3-n}$ ($n = 1, \dots, 6$) series (e.g. ligand field strength of nitro ligand, or thermodynamic stabilities) which have been observed by other authors [31,38]. These considerations will be the subject of our forthcoming report.

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REFERENCES

1. Urland, W., and Niketić, S. R., *Chem. Phys. Letters*, 1986, **129**, 529; Niketić, S. R. and Urland, W., *Polyhedron*, 1987, **6**, 947; Zarić, S. and Niketić, S. R., *Polyhedron*, 1991, **10**, 2665; Zarić, S. and Niketić, S. R., *Polyhedron*, 1991, **10**, 2673; Zarić, S., Ph. D. Dissertation, University of Belgrade, 1994; Niketić, S. R., Plenary Lecture, *4th Conf. Serbian Crystallogr. Soc.*, Novi Sad, 1994.
2. Gažo, J., Boča, R., Jona, E., Kabešova, M., Macaškova, L., Šima, J., Pelikan, P., Valach, F., *Coord. Chem. Rev.*, 1982, **43**, 87.
3. Boča, R., *Polyhedron*, 1995, **14**, 367.
4. Anisotropic π -effect is a structural effect and refers to the equilibrium properties of complexes. In some papers [5–7] structural *trans*-effect was named *trans*-influence.

5. Appleton, A. G., Clark, H. C. and Manzer, L. E., *Coord. Chem. Rev.*, 1973, **10**, 335.
6. Pidcock, A., Richards, R. E. and Venanzi, L. M., *J. Chem. Soc. A*, 1966, 1707.
7. Shustrorovich, E. M., Porai-Koshits, M. A. and Buslaev, Y. A., *Coord. Chem. Rev.*, 1975, **17**, 1.
8. Burdett, J. K. and Albright, T. A., *Inorg. Chem.*, 1979, **18**, 2112.
9. Burdett, J. K., *Molecular Shapes*, John Wiley and Sons, New York (1980).
10. Albright, T. A., Burdett, J. K. and Whangbo, M.-H., *Orbital Interactions in Chemistry*, John Wiley and Sons, New York (1985).
11. To our knowledge, crystal structures of penta-nitro complexes have not been reported.
12. The Gmelin Institute, *Inorganic Crystal Structure Database*, available through STN International, Fachinformationszentrum, Karlsruhe, Germany.
13. Bokii, G. B. and Gilinskaja, E. A., *Doklad. Akad. Nauk SSSR*, 1953, **88**, 461.
14. Wells, A. F., *Z. Kristallogr.*, 1936, **95**, 74.
15. Tanito, Y., Saito, Y. and Kuroya, H., *Bull. Chem. Soc. Jpn.*, 1952, **25**, 188.
16. Laing, M., Baines, S. and Sommerville, P., *Inorg. Chem.*, 1971, **10**, 1057.
17. Ferrari, A. and Nardelli, M., *Gazz. Chim. Ital.*, 1947, **77**, 422.
18. Adovasio, V., Lina, F., Nardelli, M. and Pelizzi, G., *Acta Cryst.*, 1994, **C50**, 671.
19. Bianchi, R., Gatti, C., Adovasio, V. and Nardelli, M., *Acta Cryst.*, 1996, **B52**, 471.
20. Cagnon, C., Matalon, J. R. and Beauchamp, A. L., *Acta Crystallogr.*, 1978, **B34**, 1128.
21. Bernal, I., *Inorg. Chim. Acta*, 1985, **96**, 175.
22. Nardelli, M., *J. Appl. Crystallogr.*, 1995, **28**, 659.
23. Burnett, M. N. and Johnson, C. K., *Ortep-III: Oak Ridge thermal ellipsoid plotting program for crystal structure illustrations*, ORNL-6895, Oak Ridge Natl. Lab., Oak Ridge, Tennessee, July 1996.
24. Komiyama, Y., *Bull. Chem. Soc. Jpn.*, 1956, **29**, 300.
25. Rau, V. G., Bondar, V. I., Ilyukhin, V. V., Struchkov, Yu. T. and Belov, N. V., *Doklad. Akad. Nauk SSSR*, 1982, **267**, 1371.
26. King, E. P., *J. Am. Statist. Assoc.*, 1958, **48**, 531.
27. van Driel, M. and Verweel, H. J., *Z. Kristallogr.*, 1939, **95**, 308.
28. Barnett, V. and Lewis, T., *Outliers in Statistical Data*, Wiley, New York (1984).
29. Hitchman, M. A. and Rowbottom, G. L., *Inorg. Chem.*, 1982, **21**, 823.
30. Hitchman, M. A. and Rowbottom, G. L., *Coord. Chem. Rev.*, 1982, **42**, 55.
31. Buist, R. J., Au-Yeung, S. C. F. and Eaton, D. R., *Can. J. Chem.*, 1985, **63**, 3567.
32. Juranić, N., Čelap, M. B., Vučelić, D., Malinar, M. J. and Radivojša, P. N., *Spectrochim. Acta*, 1979, **35**, 997.
33. Au-Yeung, S. C. F., Kwong, K. W. and Buist, R. J., *J. Am. Chem. Soc.*, 1990, **112**, 7482.
34. Chan, J. C. C. and Au-Yeung, S. C. F., *J. Chem. Soc. Faraday Trans.*, 1996, **92**, 1121.
35. Shimura, Y., *Bull. Chem. Soc. Jpn.*, 1988, **61**, 693.
36. Cooper, N. J., Pennell, C. A. and Johnson, B. C., *Inorg. Chem.*, 1983, **22**, 1956.
37. Kastner, M. E., Smith, D. A., Kuzmission, A. G., Cooper, J. N., Tyree, T. and Yearick, M., *Inorg. Chem. Acta*, 1989, **158**, 185, and references therein.
38. Herak, R., Juranić, N. and Čelap, M. B., *J. Chem. Soc. Chem. Commun.*, 1980, 660; Tomić, Z., M.Sc. Thesis, University of Belgrade, 1993.
39. Mealli, C. and Proserpio, D., *J. Chem. Educ.*, 1990, **67**, 399.
40. Brtin, O., *Acta Chem. Scand.*, 1968, **22**, 2890.
41. Podberezkaya, N. V., Virovets, A. V. and Boldyreva, E. V., *Zh. Strukt. Khim.*, 1991, **32**, 89.
42. Cotton, F. A. and Edwards, W. T., *Acta Crystallogr.*, 1968, **B24**, 474.
43. Kubota, M. and Ohba, S., *Acta Crystallogr.*, 1992, **B48**, 627.
44. Oonishi, I., Muto, F. and Komiyama, Y., *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2791.
45. Oonishi, I., Fujimaki, H., Muto, F. and Komiyama, Y., *Bull. Chem. Soc. Jpn.*, 1970, **43**, 733.
46. Nuber, B., Siebert, H., Weidenhammer, K., Weiss, J. and Zigler, M. L., *Acta Crystallogr.*, 1979, **B35**, 1020.
47. Bernal, I., Schlemper, E. O. and Fair, C. K., *Inorg. Chim. Acta*, 1986, **115**, 25.
48. Bernal, I., *Inorg. Chim. Acta*, 1985, **96**, 99.
49. Bondar, V. I., Kurkutova, E. N., Rau, V. G., Ilyukhin, V. V. and Belov, N. V., *Doklad. akad. Nauk SSSR*, 1979, **244**, 358.
50. Ohba, S., Toriumi, K., Sato, S. and Saito, Y., *Acta Crystallogr.*, 1978, **B34**, 3535.
51. Gromilov, A., Alekseev, V. I., Baidina, I. A. and Khranenko, S. P., *Zh. Neorg. Khim.*, 1992, **37**, 615.
52. Using the 'hardest' nonbonded potential available for oxygen atoms [53] ($r_0 = 3.25 \text{ \AA}$; $v = 0.10 \text{ kcal}$; and the charge of up to 0.63 a.u.) a barrier of 0.8 kcal/mol per one nitro group was found. Full details of the conformational analysis of the $[\text{Co}(\text{NO}_2)_6]^{3+}$ ion and other related structures will be presented elsewhere.
53. Hay, B. P., *Inorg. Chem.*, 1995, **34**, 569.