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Ligand-induced release of HNO/NO^- from a cobalt(II)-nitrosyl complex

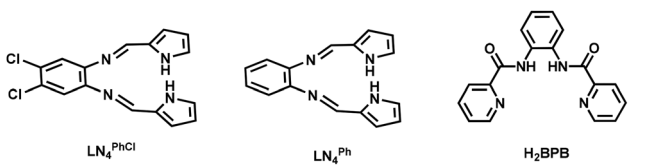
Shankhadeep Saha,[a] Bristi Maina Deka,[a] Ankur K. Guha [b] and Biplab Mondal *[a]

A Co-nitrosyl complex, [Co(TMTAA^{2-})(NO)], 1a [TMTAA^{2-} = 5,7,12,14-tetramethyldibenzotetraaza[14]annulene dianion] of {Co(NO)}^{8} configuration is shown to donate NO^- in the presence of imidazole.

Nitric oxide (NO)-driven physiological and biochemical processes are often found to involve an intermediate derived from its one electron reduction analogue known as nitroxyl or HNO/NO^-.[1–5] The endogenous production and the biological role of nitroxyl are still elusive due to its high reactivity towards itself,[6] thiol or thiolate[3] and iron-containing proteins.[4] This short-lived species instantly dimerizes and dehydrates to produce nitrous oxide (N_2O), which makes it very difficult to study extensively.[6] The advancement of HNO as a potential therapeutic agent has become a great interest for research. Its stronger vasodilative effect, compared to NO, highlights its potential as an inotropic agent for heart failure treatment.[7,8] Sources of nitroxyl are limited to a few compounds such as Angeli's salt[9] and Piloty's acid.[10] The simultaneous release of other reactive species and their functionality at strongly alkaline pH (Piloty's acid) hinder their widespread utility. Thus, for a better understanding of the biological roles and therapeutic applications of HNO/NO^-, several attempts have been made to prepare metal-nitrosyl based HNO/NO^- donor compounds.[11–21] Metal-nitrosyl complexes can serve as NO sources, with release triggered by external stimuli like light, heat or pH variations.[22–28] Metal-HNO reactivity and HNO/NO^- donation are mostly limited to iron-nitrosyl complexes of {Fe(NO)}^{8} configuration due to its highly electron-rich nature.[11–17] However, examples of cobalt nitrosyl complexes as HNO/NO^- donors are still scarce. Amongst the known cobalt nitrosyl complexes with {Co(NO)}$^{7/8/9}$ configurations, only the {Co(NO)}^{8} (considering its [Co^{III}–NO^-] electronic character) and {Co(NO)}^{9} (highly electron-rich nature) complexes are considered capable of acting as potential HNO/NO^- donors. Only a handful of such complexes have been reported.[18,19,21] HNO donation from a cobalt-nitrosyl complex was first reported by Harrop *et al.*, and it involves the proton-induced activity of a {Co(NO)}^{8} complex, [Co(LN_4^{PhCl})(NO)] (LN_4^{PhCl} = dianion of (N^1E,N^2E)-N^1,N^2-bis(1*H*-pyrrol-2-yl)methylene-4,5-dichlorobenzene-1,2-diamine).[18] Subsequently, two more analogous {Co(NO)}^{8} complexes, [Co(LN_4^{Ph})(NO)] and [Co(LN_4^{PhCl})(NO)] (LN_4^{Ph} = dianion of (N^1E,N^2E)-N^1,N^2-bis(1*H*-pyrrol-2-yl)methylene)-benzene-1,2-diamine) were reported by the same group, which upon reduction to their corresponding {Co(NO)}^{9} complexes, also act as HNO/NO^- donors.[19] Recently, our group also reported a {Co(NO)}^{8} complex, [Co(BPB^{2-})(NO)] (H_2BPB = 1,2-bis(2-pyridinecarboxamido)benzene), which shows HNO/NO^- releasing ability in the presence of anionic sixth ligands like BF_4^- (tetrafluoroborate anion), DTC^- (DTC^- = diethyldithiocarbamate anion) *etc.* (Chart 1).[21]

Herein, we report a cobalt-nitrosyl complex, [Co(TMTAA^{2-})(NO)], **1a**, (H_2TMTAA = 5,7,12,14-tetramethyldibenzotetraaza[14]annulene), which releases NO^- in the presence of a neutral sixth ligand, such as imidazole. The release is monitored *via* NO^- consumption by well-known HNO/NO^- trapping agents such as [Mn^{III}(TPP^{2-})Cl] and [Fe^{III}(TPP^{2-})Cl].

The ligand, H_2TMTAA was synthesized *via* a template synthesis method reported earlier using $Ni(OAc)_2{\cdot}4H_2O$ (Exp. Sec.).[29] Spectroscopic characterization was done to confirm the formation of the ligand (SI, Exp. Sec., Fig. S1–S4). The precursor complex **1** was synthesized from the reaction of the ligand and $Co(OAc)_2{\cdot}4H_2O$ (SI, Exp. Sec.) and was characterized using FT-IR, UV-visible, and EPR spectroscopy along with ESI-mass



LN_4^{PhCl} LN_4^{Ph} H_2BPB

Chart 1 Schematic representations of the ligand frameworks reported in ref. 18, 19 and 21.

[a] *Department of Chemistry, Indian Institute of Technology Guwahati, Assam 781039, India. E-mail: biplab@iitg.ac.in*

[b] *Department of Chemistry, Advanced Computational Chemistry Center, Cotton University, Guwahati, Assam-781001, India*

spectrometry to support its formulation (SI, Exp. Sec., Fig. S5–S8). Attempts to obtain single crystals from the isolated complex were unsuccessful due to rapid precipitation. Therefore, a slow diffusion method involving layering of $Co(OAc)_2{\cdot}4H_2O$ (MeOH) over H_2TMTAA (CH_2Cl_2) under Ar was employed, allowing gradual *in situ* complex formation and affording crystals suitable for X-ray analysis (SI, Exp. Sec., Fig. S9). The structural parameters match well with the reported ones.[30,31]

The mononitrosyl cobalt complex, [Co(TMTAA^{2-})(NO)], **1a** was synthesized by bubbling NO gas into the dry and degassed dichloromethane solution of complex **1**. The complex was isolated as a solid and was structurally characterized using standard spectroscopic methods (SI, Fig. S10–S14). In the FT-IR spectrum, the stretching frequency at 1622 cm^{-1} is assignable as the nitrosyl stretching frequency of the nitrosyl complex **1a** (SI, Fig. S10a). Upon reaction with ^{15}NO, the ν(NO) band shows a shift from 1622 cm^{-1} to 1590 cm^{-1} in the IR spectrum, which is consistent with the expected isotopic effect for NO stretching (SI, Fig. S10b). Floriani *et al.* reported nitrosyl complexes with the same H_2TMTAA ligand framework containing manganese(II) and iron(II) centres which show nitrosyl stretching frequencies at 1685 and 1636 cm^{-1}, respectively.[32] These stretching vibrations are considerably lower than the usual range of analogous complexes.[18,21,33] Although cobalt-nitrosyl complexes of {Co(NO)}^{8} configuration typically show nitrosyl-stretching frequencies in between 1660–1720 cm^{-1} (SI, Table S1), the presence of the electron-donating H_2TMTAA ligand in **1a** is perhaps responsible for the low nitrosyl stretching frequency. The diamagnetic nature of **1a** was confirmed from X-band EPR spectroscopy (SI, Fig. S12), which is further supported by the well-resolved ^{1}H NMR spectrum (SI, Fig. S13) and the cyclic voltammetry results (1st signal: E_{pa} = 0.21 V, E_{pc} = 0.16 V; 2nd signal: E_{pa} = 0.42 V, E_{pc} = 0.36 V; *vs.* Ag/AgNO$_3$, 0.1 M TBAPF$_6$ electrolyte, scan rate 0.1 V s^{-1}) (SI, Fig. S14).

The single crystal structure of complex **1a** was determined and refined in the triclinic $P\bar{1}$ space group. The ORTEP diagram of complex **1a** is shown in Fig. 1. The crystal structure reveals a non-planar saddle shape for the complex, which arises due to the steric interaction between the benzo and methyl groups of the ligand framework. The cobalt centre is five coordinated, being bonded to four equatorial ligand nitrogen atoms and one axial nitrogen atom of the nitrosyl unit to give a distorted square-pyramidal geometry. The cobalt centre is elevated from the N4 plane of the ligand towards the nitrosyl unit by 0.258 Å. The Co-N–O bond angle is 125.1(3)°. The Co–N_{ligand} bond distance is 1.902(3) Å for complex **1a**. The apical Co–N_{NO} bond length appears to be 1.818(3) Å. The observed N–O bond length is 1.124(5) Å. All the crystal parameters are in accordance with the previously reported analogous values (SI, Table S1).

Of all the transition metal nitrosyl complexes utilized as HNO donors, the {Fe(NO)}^{8} complexes are the most commonly used.[11–14] However, preparing such complexes requires the one-electron reduction of the precursor {Fe(NO)}^{7} complexes using electrochemical reduction or an external reducing agent. A similar approach was used to prepare {Co(NO)}^{9} complexes.[19] All these reduction methods are highly energy demanding and difficult to handle as the reduced metal nitrosyls are produced *in situ* and are very unstable in nature. Conversely, the low-spin {Co(NO)}^{8} complexes are very stable and can be easily isolated. Cobalt nitrosyl complexes are formally known to have a [Co^{III}-NO$^-$] electronic character. Perhaps the kinetic inertness of this low spin d^6 Co^{III} centre stabilizes the nitrosyl complexes and is also responsible for its ineffectiveness as an HNO/NO$^-$ donor.[34] However, in the present case, the strong NO$^-$ character of complex **1a** may make it a suitable candidate for nitroxyl donation. To check the NO$^-$-donating ability of complex **1a**, it was reacted with well-known nitroxyl trapping agents (Scheme 1).

Manganese(III) complexes have been used as HNO/NO$^-$ trapping agents for a long time.[15,35] Hence, the reaction of complex **1a** and [Mn^{III}(TPP^{2-})Cl] [TPP^{2-} = 5,10,15,20-tetraphenylporphyrin] (1 mole equivalent) in degassed dichloromethane solution was studied using FT-IR spectroscopy. Even after stirring the reaction mixture for over 24 hours, the FT-IR spectral pattern remains unchanged (SI, Fig. S21). Hence, to facilitate the NO$^-$ donation, a sixth ligand was introduced in the reaction mixture. Considering the nitrosyl moiety has a strong NO$^-$ character, a neutral sixth ligand was used. Thus, by carrying out the same reaction in the presence of imidazole (IM) (1 mole equivalent), the formation of a new stretching vibration at 1759 cm^{-1} along with the simultaneous disappearance of the 1622 cm^{-1} band in the FT-IR spectrum was seen (Fig. 2a). This 1759 cm^{-1} stretching frequency was identified as the

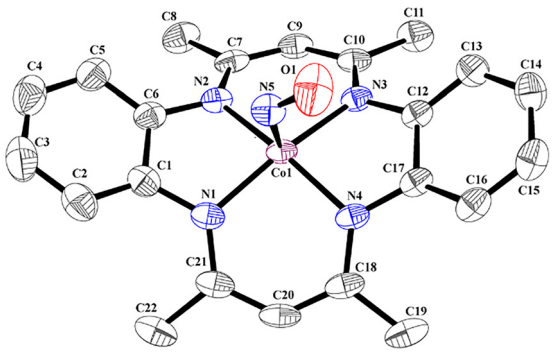
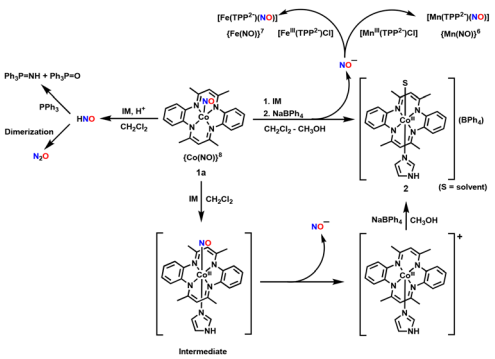


Fig. 1 ORTEP diagram of complex **1a** (H atoms and solvent are omitted for clarity).



Scheme 1 Overall reactions presented in this study.

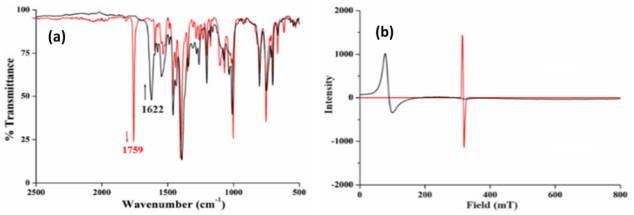


Fig. 2 (a) FT-IR (ATR) spectral monitoring of the reaction mixture of complex **1a** with [$Mn^{III}(TPP^{2-})Cl$] in the absence (black) and presence (red) of imidazole. (b) X-band EPR spectra of the reaction mixture of complex **1a** with with [$Fe^{III}(TPP^{2-})Cl$] in the absence (black) and presence (red) of imidazole. The spectra were recorded at 77 K using a microwave frequency of 9.13 GHz and a microwave power of 0.998 mW.

characteristic nitrosyl stretching of the [$Mn(TPP^{2-})(NO)$] complex.[36] The isolation and standard spectroscopic characterization also confirm the formation of the $\{Mn(NO)\}^6$ complex during the reaction (SI, Fig. S30–S32). However, in the presence of imidazole, the reaction mixture of **1a** and [$Fe^{III}(TPP^{2-})Cl$] shows a new stretching frequency at 1698 cm^{-1} in the FT-IR spectrum, which is attributed to the formation of [$Fe(TPP^{2-})(NO)$] in the reaction medium (SI, Fig. S33) with concomitant disappearance of the nitrosyl stretching frequency of **1a**. This observation demonstrates that the transfer of NO^- from complex **1a** to [$Fe^{III}(TPP^{2-})Cl$] occurs during the course of the reaction. Additionally, the X-band EPR spectroscopic study of the reaction mixture shows a sharp isotropic signal at $g \sim 2.04$, suggesting the presence of an $\{Fe(NO)\}^7$ complex (Fig. 2b).[21,37,38] The newly formed [$Fe(TPP^{2-})(NO)$] complex was isolated and characterized spectroscopically (SI, Fig. S34–S36). The effect of increasing the coordination number from five to six for a cobalt-nitrosyl complex of $\{Co(NO)\}^8$ configuration with a bis-arsenide ligand framework was demonstrated by Enemark *et al.* where the change in the electronic nature of the nitrosyl moiety from NO^+ to NO^- was observed.[39] In the presence of a sixth anionic ligand like DTC^- (diethyldithiocarbamate anion), HNO donation from a $\{Mn(NO)\}^6$ complex was also reported.[20] A $\{Co(NO)\}^8$ complex that also donates HNO/NO^- in the presence of a sixth ligand (BF_4^-, DTC^- and imidazole) was reported very recently.[21] Hence, it is logical to assume that the imidazole, as a sixth ligand for complex **1a**, facilitates the NO^- donation to suitable acceptors like [$Mn^{III}(TPP^{2-})Cl$] and [$Fe^{III}(TPP^{2-})Cl$]. To gain further insight, the reaction of imidazole with complex **1a** was studied using other spectroscopic techniques. The addition of 1.2 mole equivalents of imidazole to a dry and degassed dichloromethane solution of complex **1a** results in the quenching of the 399 nm band with the concomitant formation of a new absorption band at 446 nm in UV-visible studies (SI, Fig. S38). Monitoring the same reaction even at −40 °C does not show the formation of any intermediate. Hence, we turned to theoretical studies to check for possible intermediate formation.

The FT-IR monitoring of the reaction of complex **1a** and imidazole shows the disappearance of the nitrosyl stretching frequency at 1622 cm^{-1} (SI, Fig. S37). It is noteworthy that the formation of any oxidized or reduced product of the nitrosyl moiety was not observed in the FT-IR spectrum. Subjecting this reaction mixture to X-band EPR spectroscopy results in an EPR-silent spectrum suggesting the presence of a diamagnetic cobalt(III) centre in the newly formed species (SI, Fig. S19). These spectroscopic observations suggest that the release of the nitrosyl unit with a concomitant one electron oxidation of the cobalt centre occurs. Thus, it is reasonable to assume that the release of the nitrosyl moiety from complex **1a** occurred as NO^-. The addition of 1 mole equivalent of $NaBPh_4$ (in methanol) to the reaction mixture causes a significant change in the UV-visible spectrum (SI, Fig. S15) confirming the formation of complex [$Co^{III}(TMTAA^{2-})(IM)$][BPh_4], **2**. Complex **2** was isolated as a brown solid and characterized using various spectroscopic methods (SI, Fig. S17–S20). Although no crystal structure of complex **2** was obtained even after several attempts, a molecular ion peak at m/z = 469.155 (calculated: 469.155) in the ESI mass spectrum was observed confirming the formation of a $[Co^{III}(TMTAA^{2-})(IM)]^+$ unit (SI, Fig. S20). The formation of HNO was confirmed from its characteristic reaction with phosphines (PR_3).[40] The reaction of complex **1a**, imidazole (1.2 mole equivalents) and PPh_3 (2.5 mole equivalents) was performed in the presence of H^+ (1.5 mole equivalents) and was monitored using ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of the reaction mixture was recorded after 24 hours and shows the formation of the free base aza-ylide ($Ph_3P{=}NH$, δ_{ppm} = 21.68) and phosphine oxide ($Ph_3P{=}O$, δ_{ppm} = 28.83) (SI, Fig. S48).[18,20,21] This observation demonstrates the successful release of NO^- from complex **1a**, which converts to HNO in the presence of H^+. Although in this reaction $Ph_3P{=}NH$ and $Ph_3P{=}O$ are expected to form in equimolar quantities, the lower stability of $Ph_3P{=}NH$ resulted in a ratio of 0.64 : 1. Unreacted PPh_3 shows a signal at δ_{ppm}, −5.07. The signal at δ_{ppm}, 36.62 can be attributed to the formation of $Ph_3P{=}NH{\cdot}HBF_4$. This value is in accordance with previously reported analogous values.[41] The NO^- donation from complex **1a** was further confirmed by testing in the presence of N_2O in the headspace gas of the reaction vessel. N_2O was formed from the decomposition of hyponitrous acid ($H_2N_2O_2$), which is the dimerization product of HNO.[6] In the presence of H^+ in the reaction medium, subjecting the headspace gas of the reaction mixture of complex **1a** and imidazole to GC shows a strong signal at 2.77 minutes, suggesting the presence of N_2O (SI, Fig. S44). The GC-mass spectrum also shows a strong signal at m/z = 44 for N_2O (SI, Fig. S46). The yield of N_2O was calculated to be *ca.* 65% (0.13 mmol) using GC (SI, Fig. S45). For complex **1a**, the frontier Kohn–Sham orbitals (HOMO and LUMO) along with their energies (eV) have been calculated and are shown in the SI, Fig. S49. The HOMO–LUMO gap of complex **1a** is 4.8 eV. The HOMO in the complex has contributions from the π orbitals of the phenyl ring, the lone pairs of the N atom along with the π* orbital of the NO moiety. Participation of the Co d orbital in the HOMO is not very significant. The LUMO has a contribution mainly from the π* orbital of the phenyl ring. The imidazole-bound intermediate has been fully optimized at the M06-2X/def2-TZVP level and found to be a minimum energy structure (Fig. 3). The computed Co–N(NO) distance is 1.885 Å, the Co–N(imidazole) distance is 2.165 Å, the N–O distance is

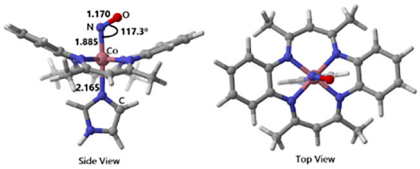


Fig. 3 Different views of the optimized local minimum geometry of the intermediate, **1b**. Bond lengths are in Å and the angle is in degrees (°).

1.170 Å and the Co–N–O angle is 117.3°. It should be noted that these are computationally calculated gas phase distances and should not be compared with solid state X-ray parameters of complex **1a**. Then, optimization was done for complex **1a**. The computed Co–N(NO) distance is 1.852 Å, the N–O distance is 1.156 Å and the Co–N–O angle is 116.7°. Thus, comparing the optimized gas phase geometries of complex **1a** with that of **1b**, it is evident that there is an elongation of the Co–N(NO) distance in **1b** compared to **1a** which perhaps induces the release of NO. The key occupied frontier orbitals representing the Co–NO (HOMO−1) and Co-imidazole (HOMO−6) interactions are depicted in the SI, Fig. S50. In the HOMO−1, the d_{z^2} orbital of Co interacts with the π* orbital of NO leading to the overlap of orbitals. This is indicated by the smaller Wiberg bond index value of 0.23 for the Co–N bond. An orbital composition analysis reveals that Co utilizes 38% of the d_{z^2} orbital. Conversely, in HOMO-6, which represents the Co-imidazole interaction, there is perfect formation of a Co–N (imidazole) σ bond (SI, Fig. S50). Orbital composition analysis reveals that Co utilizes 49% of the d_{yz} orbital and the calculated Wiberg bond index for the Co-N (imidazole) bond is higher (0.72), thus indicating a stronger Co-imidazole interaction. This indicates that the presence of imidazole makes the NO group labile and facilitates its release. This might be due to the *trans* directing effect of imidazole, which corresponds to the interaction between the d_{z^2} orbital of Co with that of the N atoms of both the NO and imidazole moieties (SI, Fig. S51). It would be worth mentioning that the influence of axial ligand on the properties of coordinated NO in the case of nitrosyl complexes of iron(II) porphyrin have been reported earlier; it was shown that the *trans* ligand weakens the Fe–NO bond.[42]

Thus, in conclusion, a penta-coordinated cobalt mononitrosyl complex, **1a**, in the presence of imidazole as a sixth ligand, was found to donate HNO/NO^-. This is confirmed by its reaction with well-known nitroxyl scavengers like Mn(III) and Fe(III) heme complexes. The release of the HNO was further confirmed by its reaction with PPh_3 and the evolution of N_2O. These results demonstrate the potential of the $\{Co(NO)\}^8$ complexes as nitroxyl donors. It would be worth to mention that other neutral sixth ligand such as morpholine has also been found to induce similar reactivity.

Conflicts of interest

There are no conflicts to declare

Data availability

Data associated with this article, including experimental procedures and compound characterization, are available in the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d6cc00661b.

CCDC 2374826 contains the supplementary crystallographic data for this paper.[43]

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