New Rhenium(I) and Rhenium(II) Species Assembled by Stereospecific Azopyridine Chelation

Suman Sengupta,[a] **Indranil Chakraborty,**[a] **and Animesh Chakravorty***[a,b]

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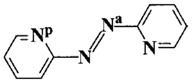
The spontaneous reaction of $[ReO(OEt)I_2(PPh_3)_2]$ with 2,2′-azobipyridine (L) in acetonitrile, and of $[ReOCl_3(PPh_3)_2]$ with L in toluene, proceeds stereospecifically furnishing the green tris-chelate $[Re^{I}L_3]I$ (**1**) and the red bis-chelate $[Re^{II}Cl_2L_2]$ (**2**), respectively. A structure determination reveals that the coordination geometry of **1** is facial and that of **2** is *cis*(Cl,Cl)-*trans*(N^p,N^p)-*cis*(N^a,N^a) (N^p is a pyridine nitrogen and N^a is an azo nitrogen). The isomer preference is exclusive in both cases and no other isomer has been observed. The average N–N distance in both compounds is about 1.35 Å, signifying the presence of strong d(Re)-π*(azo) back-bonding which plays a crucial role in controlling isomer specificity. The bis-chelate **2** is a one-electron paramagnet and displays a six-line EPR spectrum in fluid solution with $g = 2.080$ and $A = 320$ G. The ^{1}H NMR spectrum of diamagnetic **1** is consistent with the facial geometry. In acetonitrile solution **1** displays an Re^{II}/Re^{I} couple and **2** an Re^{III}/Re^{II} couple, the reduction potentials being 0.60 and 0.50V vs. SCE respectively. The violet-coloured imide complex $[Re^{V}Cl_3(NC_6H_4Cl\text{-}p)L]$ (**3**) is also reported; it displays an Re^{VI}/Re^{V} redox wave at 1.33 V vs. SCE. The stabilization of the lower rhenium oxidation states in **1** and **2** is consistent with the decrease of metal reduction potential with progressive L chelation.

Introduction

In the design of potential radiopharmaceuticals based on rhenium the higher oxidation states of the metal (especially +5) have commonly been employed, although lower states like +1 and +2 are now receiving increasing attention.[1,2] This has prompted us to investigate the synthesis and characterization of new rhenium(I) and rhenium(II) species. Herein we report the unprecedented rhenium coordination types $Re^{I}N_6$ and $Re^{II}Cl_2N_4$ in the form of **1** and **2**, respectively, assembled by 2,2′-azobipyridine (L) chelation. The compounds occur exclusively in a single geometrical form: facial in the case of **1** and *cis*(Cl,Cl)-*trans*(N^p,N^p)-*cis*(N^a,N^a) in the case of **2**.



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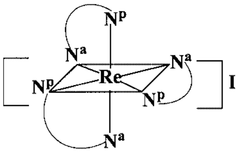

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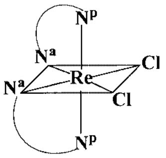

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Results and Discussion

The reaction of $[ReO(OEt)I_2(PPh_3)_2]$ with excess L in boiling acetonitrile afforded the green tris-complex $[ReL_3]I$ (**1**). On the other hand a 1:2.5 mixture of $[ReOCl_3(PPh_3)_2]$ and L reacted in boiling toluene furnishing red coloured $[ReCl_2L_2]$ (**2**). The latter displays two Re−Cl stretches ($\tilde{\nu}$ = 320, 330 cm^{-1}) in the IR spectrum corresponding to the *cis*-$ReCl_2$ moiety and is paramagnetic (1.95 μB; t_{2g}^5, $S = 1/2$) displaying a six-line EPR spectrum (^{185}Re and ^{187}Re: $I = 5/2$)[3] in dichloromethane solution (300 K) with $g = 2.080$ and $A = 320$ G. The ^{1}H NMR spectrum of diamagnetic (t_{2g}^6) **1** is consistent with a facial geometry in which the three chelate rings are equivalent in solution.

The geometries of **1** and **2** have been authenticated by an X-ray structure determination. Molecular views are shown in Figure 1 and 2.

Careful chromatographic workup during the syntheses did not reveal the presence of the meridional isomer of **1** or of any of the other theoretically possible isomers (*cis-cis-cis, trans-cis-cis, cis-cis-trans*, and *trans-trans-trans*) of **2**. Bond length data provide a clue to this geometrical specifi-

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[a] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Kolkata 700 032, India
Fax: (internat.) + 91-33/2473-2805
E-mail: icac@mahendra.iacs.res.in

[b] Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore 560 064, India

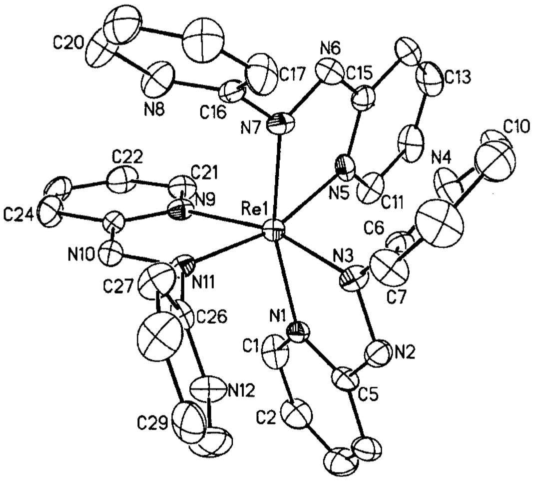

Figure 1. Perspective view and atom labeling scheme of $[ReL_3]^+$; all non-hydrogen atoms are represented by 30% thermal probability ellipsoids (hydrogen atoms are omitted for clarity); selected bond lengths [Å]: Re1−N3 1.965(9), Re1−N7 1.999(9), Re1−N5 2.111(8), Re1−N11 1.982(7), Re1−N1 2.110(8), Re1−N9 2.115(8), N2−N3 1.360(12), N10−N11 1.333(10), N6−N7 1.312(11); selected bond angles [°]: N3−Re1−N11 96.1(3), N11−Re1−N7 96.0(3), N11−Re1−N1 97.0(3), N3−Re1−N5 96.7(3), N7−Re1−N5 73.4(4), N3−Re1−N9 164.9(3), N7−Re1−N9 97.1(3), N5−Re1−N9 95.3(3), N3−Re1−N7 95.1(4), N3−Re1−N1 74.5(3), N7−Re1−N1 164.1(3), N11−Re1−N5 164.0(3), N1−Re1−N5 95.5(3), N11−Re1−N9 73.8(3), N1−Re1−N9 95.2(3)

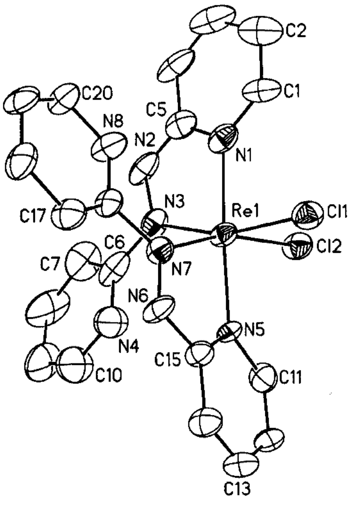

Figure 2. Perspective view and atom labeling scheme of $[ReL_2Cl_2]$; all non-hydrogen atoms are represented by 30% thermal probability ellipsoids (hydrogen atoms are omitted for clarity); selected bond lengths [Å]: Re1−N3 2.001(13), Re1−N5 2.043(10), Re1−N7 2.005(11), Re1−N1 2.080(13), Re1−Cl2 2.374(4), Re1−Cl1 2.384(4), N2−N3 1.37(2), N6−N7 1.32(2); selected bond angles [°]: N3−Re1−N7 91.8(5), N7−Re1−N5 74.4(4), N7−Re1−N1 108.3(5), N3−Re1−Cl2 93.4(4), N5−Re1−Cl2 90.3(3), N3−Re1−Cl1 163.4(4), N5−Re1−Cl1 88.6(3), Cl2−Re1−Cl1 92.25(14), N3−Re1−N5 106.9(5), N3−Re1−N1 75.0(6), N5−Re1−N1 176.8(4), N7−Re1−Cl2 164.7(3), N1−Re1−Cl2 87.0(3), N7−Re1−Cl1 86.8(4), N1−Re1−Cl1 89.7(4)

city. The average Re−N^a and Re−N^p lengths are 1.98 and 2.11 Å in **1** and 2.00 and 2.06 Å in **2**. The average N−N length in both compounds is about 0.1 Å longer than the uncoordinated azo length (1.25 Å).[4] These data clearly underline the presence of strong d(Re)-π*(azo) back-bonding in **1** and **2**. In osmium(II) bis-chelates[5,6] of azoheterocyclic ligands related to L, the N−N length is shorter by about 0.04 Å than that in **2**, signifying the π-basicity order Re^{II} > Os^{II}.

The *cis* (as opposed to *trans*) disposition of the two N^a donor sites ensures lack of competition between them for the same metal d-orbitals, thus maximizing back-bonding. In facial $[ReL_3]^+$ three *cis* ReN^a pairs are present, representing a model situation for back-bonding. This geometry is, however, more crowded (aryl groups pendant from the same face) than the unobserved meridional form which has only two *cis* ReN^a pairs. It is proposed that the stronger back-bonding more than offsets the steric disadvantage of the facial geometry which alone becomes observable. As a π-base rhenium(I) is superior to isoelectronic osmium(II) and this has a dramatic geometrical consequence. Osmium(II) tris-chelates of 2-arylazopyridines (pendant pyridine ring of L replaced by, for example, phenyl) occur primarily in the meridional form.[5]

In the case of $[ReCl_2L_2]$ the *cis-trans-cis* form is sterically more favourable than the other two possible but unobserved isomers — *cis-cis-cis* and *trans-cis-cis* — with a *cis* ReN^a pair. In the case of azoheterocyclic bis-chelates of M^{II}X$_2$ (M = Ru,[7] Os;[5,6] X = Cl, Br) isomers have been isolated and these undergo spontaneous thermal conversion into the stable *cis-trans-cis* form.[8] The stability is more critically poised for $[ReCl_2L_2]$, which occurs only in the *cis-trans-cis* form **2**.

A comment on the redox stabilization of rhenium oxidation states by L is in order here. In acetonitrile solution the nearly reversible (peak-to-peak separation 70−80 mV)

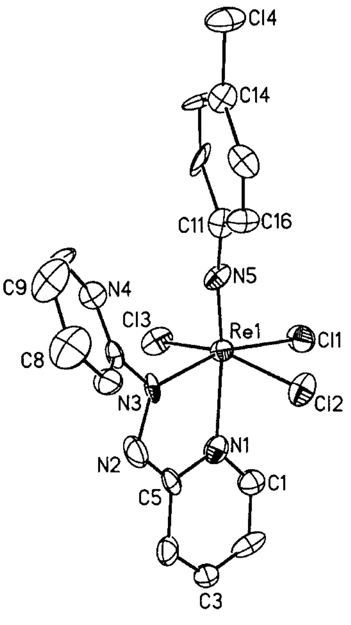

Figure 3. Perspective view and atom labeling scheme of $[ReCl_3(NC_6H_4Cl\text{-}p)L]$; all non-hydrogen atoms are represented by 30% thermal probability ellipsoids (hydrogen atoms are omitted for clarity) selected bond lengths [Å]: Re1−N5 1.72(2), Re1−N1 2.18(3), Re1−N3 2.00(2), Re1−Cl1 2.354(9), Re1−Cl2 2.386(9), Re1−Cl3 2.335(9), N2−N3 1.30(4)

cyclic voltammetric metal redox couples Re^{II}/Re^{I} in **1** and Re^{III}/Re^{II} in **2** have $E_{1/2}$ values of 0.60 and 0.50 V versus SCE respectively. No other metal redox couples are observed in the accessible potential window. On the other hand the rhenium(V) state has been realized in the violet-coloured imide complex $[ReCl_3(NC_6H_4Cl\text{-}p)L]$ (**3**; Figure 3) synthesized by reacting $[ReOCl_3(PPh_3)_2]$ with L in 1:1.5 ratio in the presence of excess $p\text{-}ClC_6H_4NH_2$.

It displays a single metal redox couple Re^{VI}/Re^{V} having an $E_{1/2}$ of 1.33V. Evidently the $E_{1/2}$ of a given Re^{n+1}/Re^{n} couple increases dramatically as the number of L chelate rings increase. The variation of this number along with coligand control provides an excellent handle for stabilizing various oxidation states of rhenium under ambient conditions. Monochelation stabilizes rhenium(V) as has also been documented for related azoheterocyclic ligands.[9,10] Tris- and bis-chelation are now shown to make the mono- and divalent states accessible in the form of **1** and **2**, respectively.

Conclusion

So far rhenium(I) compounds have been primarily known to involve[11,12] carbon monoxide, isocyanide and tertiary phosphane coordination. On the other hand, authentic mononuclear rhenium(II) compounds generally incorporate[11,13] nitrosyl/thionitrosyl and phosphane binding, with a few exceptions.[1,14] The $[ReL_3]I$ and $[ReCl_2L_2]$ chelates add a new dimension to compound types that can span the +1 and +2 oxidation states of rhenium.

Experimental Section

General: $[ReOCl_3(PPh_3)_2]$,[15] $[ReO(OEt)I_2(PPh_3)_2]$,[16] and 2,2′-azobipyridine[4] were prepared by reported methods. For electrochemical work HPLC-grade acetonitrile was used. All other chemical and solvents were of reagent grade and were used as received. Spectral measurements were made with the following equipment: IR (KBr disk), Perkin−Elmer 783 IR spectrometer; X-band EPR, Varian E-109C spectrometer. ^1H NMR, Bruker 300 MHz FT spectrometer (the proton numbering scheme used is the same as in crystallography and the assignments are based on chemical shifts, coupling constants and previous work[5]). The magnetic susceptibility was measured on a PAR 155 vibrating-sample magnetometer. Electrochemical measurements were performed under a nitrogen atmosphere using a PAR 370−4 electrochemistry system with platinum working electrode.[17] The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the potentials are referenced to the saturated calomel electrode (SCE) without junction correction.

Complex 1: L (107 mg, 0.582 mmol) was added to a solution of $[ReO(OEt)I_2(PPh_3)_2]$ (100 mg, 0.097 mmol) in acetonitrile (15 mL). The resulting mixture was heated to reflux for 3 h, affording a brownish green solution. The solvent was then removed under reduced pressure. The mass thus obtained was dissolved in a minimum amount of dichloromethane and subjected to chromatography on a silica gel column (20 × 1 cm, 60−120 mesh). A deep-green band was eluted out with a toluene/acetonitrile (1:1) mixture. Removal of solvent from the eluate gave $[ReL_3]I$ (**1**) in pure form. It was finally dried under vacuo over fused calcium chloride {**1:** 51 mg, 60% yield based on $[ReO(OEt)I_2(PPh_3)_2]$}. ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 8.12$ (d, $J = 3.7$ Hz, H1), 7.85 (complex multiplet, H2), 7.85 (complex multiplet, H3), 8.00 (d, $J = 6.0$, H4), 6.99 (d, $J = 6.0$, H7), 7.47 (t, $J = 6.0$, H8), 7.59 (t, $J = 8.7$, H9), 7.20 (d, $J = 5.6$, H10)

Complex 2: L (55.3 mg, 0.300 mmol) was added to a suspension of $[ReOCl_3(PPh_3)_2]$ (100 mg, 0.120 mmol) in toluene (25 mL). The resulting mixture was refluxed for 20 min affording a reddish solution. The solvent was then quickly removed under reduced pressure and the solid mass thus obtained was dissolved in a small amount of dichloromethane and subjected to chromatography in the same manner as mentioned above. A reddish orange band was eluted out with a toluene/acetonitrile (25:2) mixture. Solvent removal under reduced pressure afforded $[ReCl_2L_2]$ (**2**) in pure form which was dried under vacuo over fused calcium chloride {**2:** 49 mg, 65% yield based on $[ReOCl_3(PPh_3)_2]$}.

Complex 3: L (33 mg, 0.180 mmol) and *p*-chloroaniline (76 mg, 0.600 mmol) were added to a suspension of $[ReOCl_3(PPh_3)_2]$ (100 mg, 0.120 mmol) in toluene (25 mL). The mixture was heated to reflux for 2.5 h, affording a violet solution. The solvent was then removed under reduced pressure, and the mass thus obtained was subjected to chromatographic workup as before. Excess amine ($p\text{-}ClC_6H_4NH_2$) was eluted with toluene. A violet band was eluted with a toluene/acetonitrile (25:1) mixture. Solvent removal from the eluate under reduced pressure afforded $[ReCl_3(NC_6H_4Cl\text{-}p)L]$ (**3**) as a dark solid {**3:** 43 mg, 60% yield based on $[ReOCl_3(PPh_3)_2]$}.

Crystal Structure Determination: Single crystals of complexes **1**, **2** and **3** were grown by slow diffusion of hexane into dichloromethane solutions of the respective compounds. Data were collected on a Nicolet R3m/V four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) by the ω-scan technique in the range $3° \le 2\theta \le 47°$ for complexes **1** and **3** and $3° \le 2\theta \le 50°$ for **2**. All data were corrected for Lorentz-polarization and absorption.[18] The metal atoms were located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were then refined by a full-matrix least-squares procedure on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL™ V 5.03 Program package.[19] In the structure of **3** there are two very similar but crystallographically independent molecules in the asymmetric unit. Figure 3 refers to molecule 1.

Crystal Data for 1: $C_{30}H_{24}IN_{12}Re$, monoclinic, *C*2/*c* (no. 15) $a = 22.914(5)$, $b = 13.236(3)$, $c = 21.722(4)$ Å, $\beta = 110.61(3)°$, $V = 6166(2)$ Å^3, $Z = 8$, Mo-K_α ($\lambda = 0.71073$ Å), 4589 unique reflections ($R_{int} = 0.0360$). Final residuals $R_1 = 0.0391$ and $wR_2 = 0.0826$ [$I > 2\sigma(I)$], 403 parameters.

Crystal Data for 2: $C_{20}H_{16}Cl_2N_8Re$, orthorhombic, *Pbcn* (no. 60), $a = 19.190(9)$, $b = 15.431(9)$, $c = 15.062(14)$ Å, $V = 4460(5)$ Å^3, $Z = 8$, Mo-K_α ($\lambda = 0.71073$ Å), 3937 unique reflections ($R_{int} = 0.0338$). Final residuals $R_1 = 0.0603$ and $wR_2 = 0.1356$ [$I > 2\sigma(I)$], 280 parameters.

Crystal Data for 3: $C_{16}H_{13}Cl_3N_5Re$, triclinic, $P\bar{1}$ (no. 2), $a = 13.379(5)$, $b = 13.652(5)$, $c = 13.992(6)$ Å, $\alpha = 61.90(3)$, $\beta = 65.44(3)$, $\gamma = 66.12(3)°$, $V = 1980(1)$ Å^3, $Z = 4$, Mo-K_α ($\lambda = 0.71073$ Å), 5815 unique reflections ($R_{int} = 0.0368$). Final residuals $R_1 = 0.0981$ and $wR_2 = 0.2232$ [$I > 2\sigma(I)$], 464 parameters.

CCDC-192908 (**1**), -192909 (**2**) and -192910 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] G. E. D. Mullen, P. J. Blower, D. J. Price, A. K. Powell, M. J. Howard, M. J. Went, *Inorg. Chem.* **2000**, *39*, 4093−4098.

[2] J. R. Dilworth, S. J. Parrott, *Chem. Soc. Rev.* **1998**, *27*, 43−55; S. Top, H. E. Hafa, A. Vessieres, J. Quivy, J. Vaissermann, D. W. Hughes, M. J. McGlinchey, J. P. Mornon, E. Thoreau, G. Jaouen, *J. Am. Chem. Soc.* **1995**, *117*, 8372−8380.

[3] B. K. Dirghangi, M. Menon, S. Banerjee, A. Chakravorty, *Inorg. Chem.* **1997**, *36*, 3595−3601.

[4] M. Shivakumar, K. Pramanik, I. Bhattacharyya, A. Chakravorty, *Inorg. Chem.* **2000**, *39*, 4332−4338; K. Pramanik, M. Shivakumar, P. Ghosh, A. Chakravorty, *Inorg. Chem.* **2000**, *39*, 195−199.

[5] B. K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray, A. Chakravorty, *Inorg. Chem.* **1984**, *23*, 4633−4639.

[6] P. Byabartta, S. Pal, T. Misra, C. Sinha, F.-L. Liao, K. Panneerselvam, T.-H. Lu, *J. Coord. Chem.* **2002**, *55*, 479−496.

[7] R. A. Krause, K. Krause, *Inorg. Chem.* **1980**, *19*, 2600−2603; S. Goswami, A. R. Chakravarty, A. Chakravorty, *Inorg Chem.* **1981**, *20*, 2246−2250; A. H. Velders, H. Kooijman, A. L. Spek, J. G. Haasnoot, D. deVos, J. Reedijk, *Inorg. Chem.* **2000**, *39*, 2966−2967.

[8] T. Bao, K. Krause, R. A. Krause, *Inorg. Chem.* **1988**, *27*, 759−761; A. K. Deb, M. Kakoti, S. Goswami, *J. Chem. Soc., Dalton Trans.* **1991**, 3249−3251; T. K. Misra, D. Das, C. Sinha, P. Ghosh, C. K. Pal, *Inorg. Chem.* **1998**, *37*, 1672−1678.

[9] I. Chakraborty, S. Bhattacharyya, S. Banerjee, B. K. Dirghangi, A. Chakravorty, *J. Chem. Soc., Dalton Trans.* **1999**, 3747−3753.

[10] S. Banerjee, S. Bhattacharyya, B. K. Dirghangi, M. Menon, A. Chakravorty, *Inorg. Chem.* **2000**, *39*, 6−13.

[11] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley and Sons, Inc., 5th Edn., **1999**.

[12] M. L. Kuznetsov, A. J. L. Pombeiro, A. I. Dementlev, *J. Chem. Soc., Dalton Trans.* **2000**, 4413−4421; K. Wang, L. Huang, L. Gao, L. Jin, C. Hoang, *Inorg. Chem.* **2002**, *41*, 3353−3358.

[13] A. Voigt, U. Abram, R. Kirmse, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1658−1663; M. Goeldner, A. Kienast, H. Homborg, *Z. Anorg. Allg. Chem.* **1998**, *624*, 141−146.

[14] M. Stebler, A. Gutierrez, A. Ludi, B. Hans-Beat, *Inorg. Chem.* **1987**, *26*, 1449−1451.

[15] J. Chatt, G. A. Rowe, *J. Chem. Soc.* **1962**, 4019−4033.

[16] G. Francociani, G. D'Alfonso, P. Romiti, A. Sironi, M. Freni, *Inorg. Chim. Acta* **1983**, *72*, 29−37.

[17] A. Pramanik, N. Bag, D. Ray, G. K. Lahiri, A. Chakravorty, *Inorg. Chem.* **1991**, *30*, 410−417.

[18] A. C. T. North, D. C. Philips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351−359.

[19] G. M. Sheldrick, SHELXTL™ V 5.03, Bruker analytical X-ray systems, Madison, WI, 1994.

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