Multifunctional Dithiocarbamates as Ligands Towards the Rational Synthesis of Polymetallic Arrays: An Example Based on a Piperizine-Derived Dithiocarbamate Ligand

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The zwitterionic piperazine-derived dithiocarbamate complex [(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)] has been prepared and utilised in the synthesis of multimetallic arrays incorporating a wide range of transition metal centres.

Introduction

Dithiocarbamates are extremely versatile ligands which form complexes with all the transition metals, leading to the stabilisation of a wide range of oxidation states.[1] Since their complexes are easily prepared and manipulated, a wide range of applications have been developed in areas as diverse as materials science, medicine and agriculture. Given this versatility, their well-defined architecture and the bountiful metal-centred electrochemistry shown by these complexes,[2] it is surprising that they have found little use in the burgeoning area of supramolecular chemistry. Recently, however, Beer and co-workers have started to address this issue, preparing a range of exciting new supramolecular architectures based on multifunctional dithiocarbamate ligands, many of which show interesting structural-redox properties.[3] It is clear from this work that dithiocarbamates have the potential to be utilised to a far greater extent than found currently in the areas of supramolecular chemistry and materials science. With this in mind we have focused our initial efforts on the development of multidentate dithiocarbamate ligands for the synthesis of multimetallic arrays. Such arrays could be one, two or three-dimensional in nature, the dimensionality being easily controlled as a function of the properties of both the metal and ligand. We envisage that these materials will show novel physical properties in their own right and will be explored as precursors to the synthesis of well-defined nanoparticulates in a manner developed extensively by O'Brien and co-workers.[4]

Results and Discussion

A simple strategy for the synthesis of multimetallic wires is outlined below (Scheme 1). It centres on the use of a molecule containing two secondary amine centres. Such species react with CS$_2$ to afford a zwitterionic product,[5,6] whereby one of the amines acts as a nucleophile and the second as a base. Under the right conditions, only small amounts of the symmetrical double salt [S$_2$CN(X)-NCS$_2$][H$_2$N(X)NH$_2$] (X = spacer) are formed, which is a key advantage of this approach as this allows one end of the amine to be extended selectively by reaction with carbon disulfide. Reaction of the zwitterionic product, [H$_2$NC$_4$H$_8$NCS$_2$], with a metal complex results in the formation of a new metal-amine compound, which in turn can react with further CS$_2$ to generate a new metal-containing dithiocarbamate ligand. In this manner multimetallic arrays can be constructed in a modular, step-wise fashion (Scheme 1). This approach, which is demonstrated by the reactions shown in Scheme 2, can be extended using tri- and tetradentate amines to incorporate further dimensionality.

As a proof of concept, we have used cheap and commercially available piperazine in order to demonstrate the ease and potential of such an approach. We have used the ruthenium(II) complex *cis*-[RuCl$_2$(dppm)$_2$][7] to provide a *cis*-Ru(dppm)$_2$ moiety as the initial metal fragment. This choice was based on our observation that *cis*-[RuCl$_2$(dppm)$_2$] reacts cleanly with a wide range of dithiocarbamate salts to afford the cations [Ru(S$_2$CNR$_2$)(dppm)$_2$]$^+$ in high yield. These complexes are easily characterised by a range of spectroscopic techniques, of which ^{31}P NMR spectroscopy proves particularly useful.

Addition of CS$_2$ to piperazine in water results in the formation of the zwitterion, H$_2$NC$_4$H$_8$NCS$_2$ (**1**), which is readily isolated (Scheme 2). Addition of one equivalent of *cis*-[RuCl$_2$(dppm)$_2$] to this zwitterion, followed by an excess of NaBF$_4$ affords [(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NH$_2$)][BF$_4$]$_2$ (**2**) in high yield,[8] which is then converted into the new complex, [(dppm)$_2$Ru(S$_2$CNC$_4$H$_8$NCS$_2$)] (**3**), upon sequential addition of two equivalents of base and CS$_2$. The latter is a

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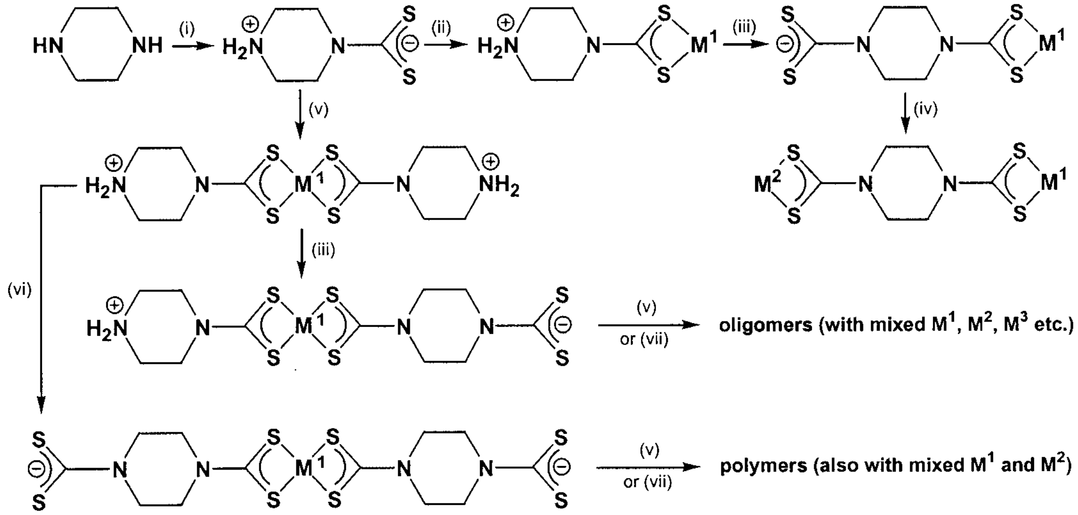
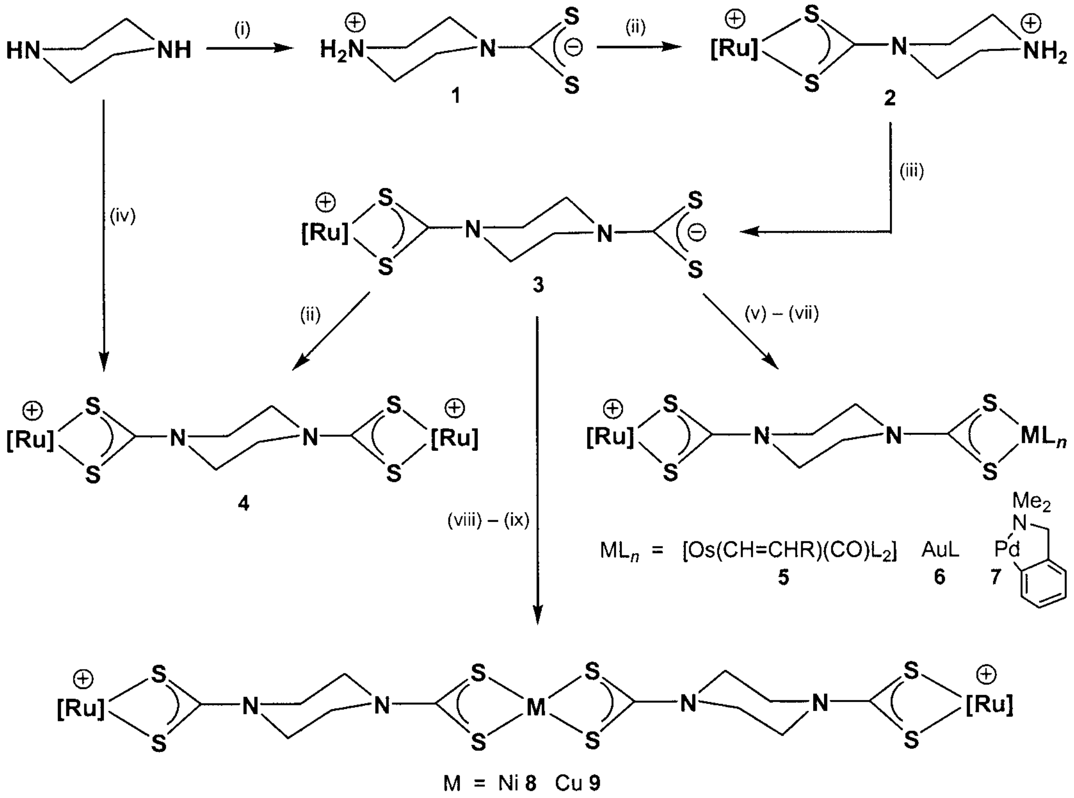


Scheme 1. (i) CS_2; (ii) M^1X; (iii) $2NEt_3$, CS_2; (iv) M^2X; (v) M^1X_2; (vi) $4NEt_3$, $2CS_2$; (vii) M^2X_2.



Scheme 2. [M] = $Ru(dppm)_2$;L = PPh_3; R = C_6H_4Me-4; (i) CS_2; (ii) *cis*-[$RuCl_2(dppm)_2$], $2NaBF_4$; (iii) $2NEt_3$, CS_2; (iv) $2NEt_3$, $2CS_2$; 2*cis*-[$RuCl_2(dppm)_2$]; (v) [$Os(CH{=}CHR)Cl(CO)(BTD)L_2$] (BTD = 2,1,3-benzothiadiazole); (vi) ClAuL; (vii) [$Pd(C_6H_4CH_2NMe_2)Cl]_2$; (viii) $Ni(OAc)_2$; (ix) $Cu(OAc)_2$.

key building block and can be considered to be a metallodithiocarbamate. In order to demonstrate its utility we treated this compound with a second equivalent of *cis*-[$RuCl_2(dppm)_2$] to afford (after salt metathesis) the binuclear complex [$(dppm)_2Ru(S_2CNC_4H_8NCS_2)Ru(dppm)_2$]-[$BF_4$]$_2$ (**4**).[9] The same complex is also produced in a one-step reaction upon addition of $Na_2[S_2CNC_4H_8NCS_2]$ to two equivalents of *cis*-[$RuCl_2(dppm)_2$] followed by salt metathesis. In order to confirm the bridging nature of the dithiocarbamate, a crystallographic study of **4** was performed (Figure 1).[10] The bridging dithiocarbamate mode found in **4** is rare but not unique; Shaver and co-workers having recently prepared a related diruthenium complex, [$Cp(PPh_3)$-$Ru(S_2CNC_6H_4NCS_2)Ru(PPh_3)Cp$], from the unusual reaction of two equivalents of [$CpRu(PPh_3)_2SH$] with *para*-phenylenediisothiocyanate.[11] A dinuclear tin complex has

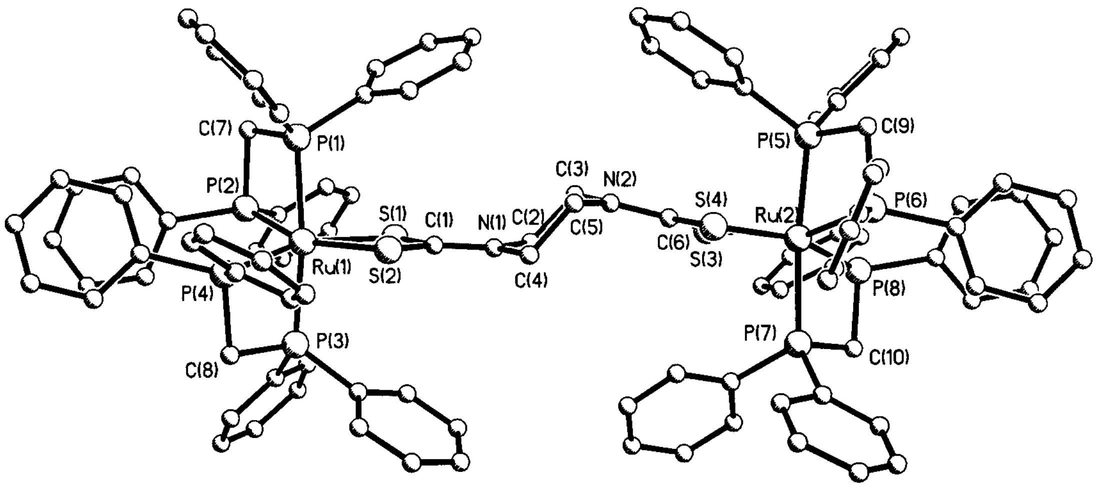


Figure 1. Structure of the cation in $[\{Ru(dppm)_2\}_2(S_2CNC_4H_8NCS_2)][BF_4]_2$ (**4**).

also been reported.[6a] Zwitterion **3** can be employed to prepare a wide range of dithiocarbamate-bridged binuclear metal complexes as we have illustrated with the formation of **5**–**7**,[9] in which osmium,[8] gold and palladium centres, respectively, are coordinated using suitable reagents.

In each of the cases described above, the added metal centre binds only a single dithiocarbamate ligand. Trimetallic units based on two bidentate dithiocarbamate ligands result from the addition of metals with two dithiocarbamate-binding sites. In order to illustrate this, we treated **3** with nickel and copper acetate to quantitatively afford $[\{(dppm)_2Ru(S_2CNC_4H_8NCS_2)\}_2M][BF_4]_2$ [M = Ni (**8**), Cu (**9**)] (Scheme 2).[9] These examples illustrate the ease of incorporation of diamagnetic and paramagnetic centres which show well-defined and understood redox properties into these arrays. We have extended this strategy to the formation of tetranuclear complexes upon coordination of zwitterion **3** to Fe^{III}, Co^{III} and La^{III} centres and are currently using methyl-substituted piperazines to prepare chiral materials. We have also begun work using 1,4,7-triazacyclononane and 1,4,8,11-tetraazacyclotetradecane (cyclam) as a building block to prepare multidentate dithiocarbamate ligands with the aim of preparing magnetic 2D sheet-like structures with large cavities.

Conclusions

The piperazine-based dithiocarbamate complexes reported here demonstrate how the construction of multimetallic arrays can be achieved in a controlled, stepwise manner. This approach has great potential for the fabrication of materials incorporating a wide range of metal centres whose properties (e. g., redox, CVD, host-guest chemistry) can be tailored.

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[8] Representative syntheses: a) Zwitterion **1** (26 mg, 0.161 mmol) and $NaBF_4$ (23 mg, 0.210 mmol) were suspended in methanol (20 mL) and *cis*-$[RuCl_2(dppm)_2]$ (100 mg, 0.106 mmol) added as a dichloromethane (10 mL) solution. The reaction was heated at reflux for 10 min and then stirred for 2 h. All solvent was removed and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Addition of ethanol (30 mL) and reduction of solvent volume by rotary evaporation yielded complex **2** (93 mg, 73%). b) Complex **2** (100 mg, 0.083 mmol) was dissolved in dichloromethane (10 mL) and treated with NEt_3 (5 drops, excess) and stirred for 5 min. Carbon disulfide (3 drops, excess) was added and the reaction stirred for 5 min to generate complex **3**. $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ (86 mg, 0.083 mmol) was added as a dichloromethane solution (10 mL) and the reaction was stirred for 1 h. All solvent was removed

and the residue was taken up in a minimum amount of dichloromethane and filtered through diatomaceous earth. Addition of ethanol (30 mL) and reduction of solvent volume by rotary evaporation yielded complex **5** (121 mg, 71%).

[9] Characterisation data for new complexes. **1**: IR (KBr/nujol): $\tilde{\nu}$ = 1601 [ν(CS)], 1580, 1265, 1227, 1207, 1134, 1119, 1015, 966, 897 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.88 (m, 4 H, H_2CNH$_2$CH_2), 4.30 (s, 2 H, NH$_2$), 4.31 [m, 4 H, H_2CN(CS$_2$)CH_2] ppm. MS(EI): m/z = 162 [M]$^+$. $C_5H_{10}N_2S_2$ (162.28): calcd. C 37.0, H 6.2, N 17.3; found C 37.7, H 6.5, N 17.5. **2**: IR (KBr/nujol): $\tilde{\nu}$ = 1585, 1574, 1312, 1269, 1236, 1190, 1161, 1057 [ν(BF)], 918, 849 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = –3.8, –17.3 [2 t, J_{PP} = 34.4 Hz, dppm] ppm. ^{1}H NMR (CDCl$_3$): δ = 2.35 [br. s, 2 H, NH$_2$], 3.04, 3.88 [2m, 2×4 H, NC$_4$H$_8$N], 4.53, 4.91 [2 m, 2×2 H, PCH$_2$P], 6.48–7.57 [6 m, 40 H, C$_6$H$_5$] ppm. FAB-MS: m/z (abundance) = 1030 (100) [M]$^+$. $C_{55}H_{53}BF_4N_2P_4RuS_2 \cdot 0.5CH_2Cl_2$ (1160.41): calcd. C 57.5, H 4.7, N 2.4; found C 57.8, H 4.6, N 2.5 (this recrystallised material was analysed as the deprotonated monotetrafluoroborate salt, [dppm$_2$Ru(S$_2$CNC$_4$H$_8$NH)]BF$_4$). **4**: IR (KBr/nujol): $\tilde{\nu}$ = 1614, 1574, 1310, 1278, 1219, 1057 [ν(BF)], 918, 849 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = –4.1, –16.8 [2 t, J_{PP} = 34.2 Hz, dppm] ppm. ^{1}H NMR (CDCl$_3$): δ = 3.51, 3.62 [2 d, J_{HH} = 9.5 Hz, 8 H, ax/eq-NC$_4$H$_8$N], 4.56, 4.91 [2 m, 2×4 H, PCH$_2$P], 6.50, 6.93, 7.03, 7.26, 7.38, 7.63 [6 m, 80 H, C$_6$H$_5$] ppm. FAB-MS: m/z (abundance) = 2063 (20) [M + BF$_4$]$^+$, 1976 (13) [M]$^+$. $C_{106}H_{96}B_2F_8N_2P_8Ru_2S_4 \cdot CH_2Cl_2$ (2234.68): calcd. C 57.5, H 4.4, N 1.3; found C 57.3, H 4.6, N 1.3. **5:** IR (KBr/nujol): $\tilde{\nu}$ = 1898 [ν(CO)], 1614, 1310, 1217, 1188, 1057 [ν(BF)], 918, 847 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 9.3 [s, PPh$_3$], –4.4, –17.1 [2 t, J_{PP} = 34.4 Hz, dppm] ppm. ^{1}H NMR (CDCl$_3$): δ = 2.21 (s, 3 H, CH$_3$), 2.78–3.33 (m br., 8 H, NC$_4$H$_8$N), 4.64, 4.97 (2 m, 2×2 H, PCH$_2$P), 5.59 [d, J_{HH} = 17.1 Hz, 1 H, Hβ], 6.36, 6.81 [(AB)$_2$, J_{AB} = 8.0 Hz, 4 H, C$_6$H$_4$], 6.52, 6.93, 6.96, 7.26, 7.61 [5m, 70 H, C$_6$H$_5$], 8.28 [dt, J_{HH} = 17.1, J_{HP} = 2.6 Hz, 1 H, Hα] ppm. FAB-MS: m/z (abundance) = 1967 (38) [M]$^+$. $C_{102}H_{91}BF_4N_2OOsP_6RuS_4 \cdot CH_2Cl_2$ (2137.97): calcd. C 57.9, H 4.4, N 1.3; found C 57.7, H 4.5, N 1.3. **6**: IR (KBr/nujol): $\tilde{\nu}$ = 1585, 1572, 1310, 1277, 1207, 1155, 1055 [ν(BF)], 912, 849 cm^{-1}. ^{31}P{^{1}H} NMR ([D$_6$]acetone): 37.5 [br. s, PPh$_3$], –3.0, –18.0 [2 t, J_{PP} = 34.5 Hz, dppm] ppm. ^{1}H NMR ([D$_6$]acetone): δ = 3.73, 3.92, 4.14, 4.23 (4 m, 8 H, NC$_4$H$_8$N), 4.75, 5.36 (2 m, 2×2 H, PCH$_2$P), 6.69, 7.00, 7.24, 7.40, 7.60, 7.63 (6 m, 55 H, C$_6$H$_5$) ppm. FAB-MS: m/z (abundance) = 1566 (3) [M]$^+$. $C_{74}H_{67}AuBF_4N_2P_5RuS_4$ (1652.33): calcd. C 53.8, H 4.1, N 1.7; found C 54.0, H 4.0, N 1.6. **7**: IR (KBr/nujol): $\tilde{\nu}$ = 1574, 1308, 1278, 1219, 1157, 1055 [ν(BF)], 907, 849 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = –4.2, –16.9 (2 t, J_{PP} = 34.2 Hz, dppm) ppm. ^{1}H NMR (CDCl$_3$): δ = 2.92 [s, 6 H, CH$_3$], 3.71, 3.79 (2 m, 8 H, NC$_4$H$_8$N), 4.01 (s, 2 H, CCH$_2$), 4.64, 4.96 (2 m, 2×2 H, PCH$_2$P), 6.53, 6.94, 7.03, 7.17, 7.31, 7.62 (6 m, 40 H + 4 H, C$_6$H$_5$ + C$_6$H$_4$) ppm. FAB-MS: m/z (abundance) = 1346 (12) [M]$^+$. $C_{65}H_{64}BF_4N_3P_4PdRuS_4 \cdot 0.5CH_2Cl_2$ (1476.16): calcd. C 53.3, H 4.4, N 2.9; found C 53.1, H 5.0, N 3.2. **8**: IR (KBr/nujol): $\tilde{\nu}$ = 1614, 1559, 1308, 1279, 1221, 1192, 1057 [ν(BF)], 910, 849 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = –4.2, –16.8 (2 t, J_{PP} = 34.5 Hz, dppm) ppm. ^{1}H NMR (CDCl$_3$): δ = 3.58 (m, 16 H, NC$_4$H$_8$N), 4.64, 4.98 (2m, 2×4 H, PCH$_2$P), 6.52, 6.94, 7.03, 7.18, 7.26, 7.38, 7.61 (7 m, 80 H, C$_6$H$_5$) ppm. FAB-MS: m/z (abundance) = 2271 (9) [M]$^+$. $C_{112}H_{104}B_2F_8N_4NiP_8Ru_2S_8$ (2444.84): calcd. C 55.0, H 4.3, N 2.3; found C 55.4, H 4.2, N 2.2. **9**: IR (KBr/nujol): $\tilde{\nu}$ = 1585, 1572, 1310, 1279, 1221, 1157, 1057 [ν(BF)], 910, 849 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = –4.2, –16.8 (2t, J_{PP} = 34.3 Hz, dppm) ppm. ^{1}H NMR (CDCl$_3$): δ = 4.61, 4.96 (2 br. s, 2×4 H, PCH$_2$P), 6.52, 6.93, 7.03, 7.32, 7.62 [5 br. s, 80 H, PC$_6$H$_5$] ppm (NC$_4$H$_8$N not observed due to effect of paramagnetism). FAB-MS: m/z (abundance) = 2276 (3) [M]$^+$. $C_{112}H_{104}B_2CuF_8N_4P_8Ru_2S_8 \cdot CH_2Cl_2$ (2534.63): calcd. C 53.6, H 4.2, N 2.2; found C 53.4, H 4.2, N 2.2.

[10] Single crystals of **4** were grown by slow evaporation of a concentrated solution of the complex in chloroform. Crystal data for **4**: [{Ru(dppm$_2$(S$_2$CNC$_4$H$_8$NCS$_2$)][BF$_4$]$_2$·3CHCl$_3$, $C_{109}H_{99}B_2Cl_9F_8N_2P_8Ru_2S_4$, M = 2507.71, monoclinic, space group $P2_1/n$, a = 22.2606(14), b = 22.2816(14), c = 22.5341(14) Å, β = 80.1650(10)°, U = 11012.7(12) Å^3, Z = 4, T = 150(2) K, μ(Mo-K_α) = 0.747 mm^{-1}, $D_{\text{calcd.}}$ = 1.512 g cm^{-3}, 26374 independent reflections measured, 10556 $I \geq 2\sigma(I)$, R_1 = 0.1020, R_w = 0.1675. Data reduction and refinement were carried using the SHELXTL PLUS V6.10 program package. The supplementary crystallographic data for this structure, CCDC-266476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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